THE SEPARATION OF NEODYMIUM AND PRASEODYMIUM BY ION EXCHANGE I. EFFECT OF COLUMN LENGTH, LOADING, AND pH OF ELUENT

A THESIS

Presented to

the Faculty of the Division of Graduate Studies

Georgia Institute of Technology

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Chemical Engineering

by

William Nelson Johnson

June 1950

THE SEPARATION OF NEODYMIUM AND PRASEODYMIUM BY ION EXCHANGE. I. EFFECT OF COLUMN LENGTH LOADING, AND pH OF ELUENT.

Approved:

Date Approved by Chairman June 27, 1950

ACKNOWLEDGEMENTS

I wish to thank Dr. W. T. Ziegler for his invaluable aid, guidance, and encouragement in the prosecution of this problem as well as for his suggestion of it. I also wish to express my thanks to Mr. J. T. Roberts, Jr. and Mr. F. LaFond for experimental information aiding and verifying my experiments. Last, but by no means least, I wish to express my gratitude to my wife for her help and encouragement in the long hours required at the laboratory in the gathering of data.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

FOREWORD

It is felt that a word of explanation regarding the organization of this thesis would enable the reader to more clearly understand the material which it contains.

The main body of the thesis contains a general discussion of experimental procedure and of materials used in the work. This discussion is intended primarily to give the reader the background for the discussion of results which follows. For the reader who is interested in the details of procedure for comparison of this work with that of other experimentalists or for the reproduction of this work, the details, concerning the materials used and the procedures followed, are presented in Appendix I.

The actual details of the column operation are presented in Appendix II. This includes such information as volume of fractions, weight of oxide obtained per fraction, pH of effluent, color of oxides obtained, average flow rates, and loadings used.

Abstract from Thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering in 1950.

THE SEPARATION OF NEODYMIUM AND PRASEODYMIUM BY ION EXCHANGE

I. EFFECT OF COLUMN LENGTH, LOADING AND pH OF ELUENT.

A study was made of the effect of pH of eluent, column length, and loading upon the separation of neodymium, and praseodymium from a mixture of oxides containing approximately 12% Nd_2O_3 , 45.1% Pr_6O_{11} , 4.7% CeO_2 , and 38.2% La_2O_3. A 120 cm. Dowex 50 resin column (approximately 4.7 cm. in diameter) was used to make the following runs and the results compared to determine the effect of pH of eluent and loading.

Run	pH of eluent	loading	Composition of oxide mixture
27*	3.12	30 gms.	45.1% Pr_6O_{11}
28	3.12	15 gms.	12.0% Nd_2O_3
30	3.00	30 gms.	38.2% La_2O_3
31	3.00	15 gms.	4.7% CeO_2
33	3.12	3.6 gms.	100% Nd_2O_3
34	3.12	30 gms.	12% Nd_2O_3 88% La_2O_3

To determine the effect of column length, the results of the above runs were compared with the results of runs made previously under similar conditions except for the use of

---

* These runs were numbered so as to be in accordance with a continuing series of experiments concerning the same general topic. This series of experiments is being carried out in the Low Temperature Laboratory of the State Engineering Experiment Station.

a 73 cm. resin column for the earlier runs.

The greatest effect was found upon variation of pH of the eluent. This effect was such as to indicate that in general an optimum pH exists for the separation of neodymium and praseodymium between 3.00 and 3.12 on a Dowex 50 resin column. The effect of pH was found to be rather critical and to be the primary variable of the three variables studied.

Increasing the column length had no appreciable effect upon the separation of components. No general conclusions could be drawn as to the effect of this variable since slight effects may have been obscured by errors within experimental limits and since data was obtained for only two different lengths of resin column. However, for practical separations of the particular mixture of rare earths studied, the shorter (73 cm.) column is recommended.

A reduction in loading gave better separation at a pH away from the optimum but had only a very slight effect, if any, when separation was already high. A possible effect of loading on the shape of the praseodymium curve was observed but further experimentation will be required to establish this effect definitely.

SEPARATION OF NEODYMIUM AND PRASEODYMIUM BY ION EXCHANGE I. EFFECT OF COLUMN LENGTH, LOADING AND pH OF ELUENT

I

INTRODUCTION

In 1949 experimental work with the rare earth oxides in the low temperature laboratory of the State Engineering Experiment Station led to a search for a suitable method of separating neodymium, praseodymium and lanthanum from a mixture of their oxides. At that time the technique of ion exchange was chosen as the most promising method of separation. Experiments were undertaken by W.T. Ziegler[1], et al., utilizing the properties of the synthetic exchange resin, Dowex 50.[2] In the period of time between the start of this work and the formulation of the plan of this thesis, some twenty four runs had been made under conditions based principally upon the results obtained by Spedding[3] and his coworkers using

---

[1] Blomeke, J.O., Roberts, J.T. Jr., and Ziegler, W.T., Paper presented before George section - American Chemical Society, Meeting in Miniature, November 17, 1949.

[2] Bauman, W.C., and Eichorn, J., J. Am.Chem. Soc., 69, 2830, (1947).

[3] Spedding,F.H., Voigt, A.F., Gladrow, E.M., and Sleight, N.R., J.Am. Chem.Soc. 69, 2777, 2786, and 2812. (1947).

Amberlite resins and those of Harris and Tompkins[4] using Dowex 50. These experiments showed complete separation of lanthanum from the other two rare earths but only incomplete separation of neodymium from praseodymium. Furthermore, these experiments raised questions which pointed the way to the experiments carried out in this thesis and to others now in process at the Experiment Station.

In a comparison of three runs made under similar conditions, except for pH of the eluent solution, it had been observed[1] that as the pH of eluent was raised successively from 2.90 to 3.00 and 3.12, the trailing edge of the praseodymium elution curve tended to shorten and the peak height to increase, giving the effect of a narrower, sharper band with each increase of pH (see Figure 1). On the other hand, while the neodymium curve exhibited a shortening trailing edge for the same pH changes, the curve appeared to become narrower and sharper for the change from pH 2.90 to 3.00 but to reverse the change and become broader and lower for the change of pH from 3.00 to 3.12. The question was raised as to the possibility of this effect being due to the excess of acid known to be present in the adsorbate solution, thus giving the effect of an acid front limitation.[5]

---

[4]Harris, D.H. and Tompkins, E.R., J.Am. Chem. Soc. 69, 2792 (1947).

[5]Tompkins, E.R., Harris, D. H., and Khyn, J. X. J. Am Chem. Soc. 71, 2504, (1949).

FIGURE 1

EFFECT OF pH OF ELUENT

RUN	pH	Resin bed Dowex 50
21	2.90	NH_4- form
23	3.00	4.7 cm- diam - 73± 2 cm. long
24	3.12	Loading - 30.0 gm oxide.
		Comp: 10.5% Nd_2O_3; 45.6% Pr_6O_{11} 43.9% La_2O_3

Volume of Fractions = 1000 ± 100 ml.

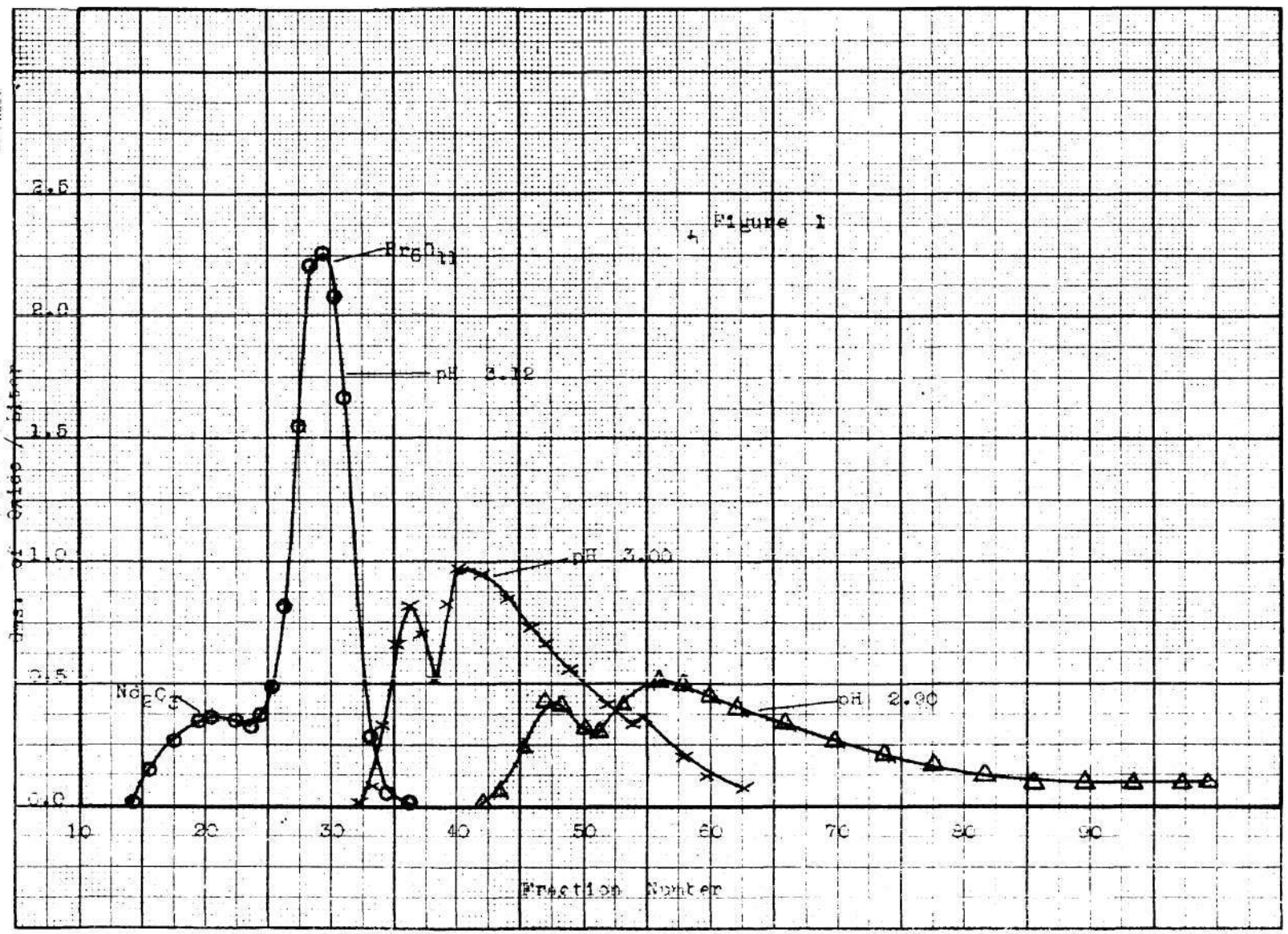


Figure 1
Fe(III)
pH 2.12
pH 3.00
pH 2.90
NaCl
2.5
2.0
1.5
1.0
0.5
0.0
10
20
30
40
50
60
70
80
90
Fraction Number

To study further the effect of pH of eluent upon the separation of neodymium and praseodymium, it was decided that the following column runs should be made:

pH	3.12	30 gm. oxide loading
pH	3.00	30 gm. oxide loading
pH	3.12	15 gm. oxide loading
pH	3.00	15 gm. oxide loading

These runs were to be made on a longer resin column (120 cm) than that used heretofore since the general theory of ion exchange suggested that greater separation of peaks might be obtained in this way. The work of Spedding, et al.[6], bears out this indication. In addition, the adsorbate solution of rare earth chlorides was to be neutralized with dilute ammonium hydroxide to eliminate insofar as possible the effect of acid front limitation. From these experiments it was expected that information might be drawn concerning the effect of loading and of column length as well as the effect of pH of eluent on the separation of neodymium and praseodymium.

---

[6]Spedding, et al., J. Am. Chem. Soc., 69, 2777 and 2786, (1947).

CHAPTER II

GENERAL THEORETICAL BACKGROUND

Before undertaking a discussion of the specific results of the group of experiments, the general aspects of the ion exchange process will be briefly reviewed. The first step in a separation of mixed cations is to adsorb these ions onto the resin. This is accomplished simply by allowing the solution of the ions to flow through the bed under such conditions that the ions to be absorbed have a greater affinity for the resin than the ions already on the resin. In the present application the adsorption of ions actually means that they displace other ions which have been held to the resin principally by electrovalent forces, the resin being an aromatic hydrocarbon polymer with the replaceable ions being attached to nuclear sulfonic groups. The affinity of cations for the cation exchanger increases with the positive charge of the ion (i.e. Monopositive < dispositive< tripositive) and ions having the same charge, increases with decreasing hydrated ionic radius or with increasing basicity.[1] The cations are adsorbed until the mass action equilibrium between rare earth ions on the resin and rare earth ions in solution is attained; i.e.,

$$M^{+n} + n\ NH_4R \rightleftharpoons n\ NH_4^{+} + MR$$

---

[1] Nachod, F.C., Ion Exchange Theory and Application, p.175 and 192., Academic Press, Inc., New York, N.Y.(1949)

That this process is limited initially to the top part of the bed has been demonstrated by Spedding[2] who concluded that the length of column occupied was directly proportional to the weight of starting material.

After the initial adsorption of the ions from their salt solution, a complexing agent is passed through the column. In this instance the complexing agent is citric acid containing varying amounts of ammonium hydroxide added to obtain the desired pH. An explanation of the manner in which the elution occurs has been given by Harris and Tompkins[3] on the basis of simple mass action reactions. The reactions taking place or in equilibrium are:

$$n\ NH_4^+ + MR_n \rightleftharpoons M^{+n} + n\ NH_4R \quad (1)$$

And

$$M^{+n} + y\ H_xCit^{x-3} \rightleftharpoons M(H_xCit)_y^{-z} \quad (2)$$

where M^{-n} is the rare earth cation, H_xCit^{x-3} some citrate ion (principally H_2Cit^- at pH's used here), R the resin ion, and z representing the charge on the complex ion = n - y (x-3). Equation (1) would only proceed a small way toward completion were it not for the reaction represented by equation (2) which effectively removes the M^{-n} ions from solution, thereby allowing more M^{-n} ions to be removed from the resin. Further, the amount of citrate ions present, and hence the

---

[2]Spedding, F.H., et al., J.Am.Chem.Soc. 69,2786 (1947)

[3]Harris, D.H. and Tompkins, E.R., J.Am.Chem. Soc.69, 2792, (1947).

[4]Nachod, F.C., Ion Exhange Theory and Application, p.179 Academic Press Inc., New York, N.Y. (1949).

degree of completion of equation (2), is dependent upon the pH of the eluent because of the equilibrium reaction:

$$H_3Cit \rightleftharpoons (3-x)\ H^+ + H_xCit^{x-3}$$

When, however, these complex ions reach the pure NH_4R below the adsorbed band, the equations above are reversed and the ions are readsorbed onto the resin, due simply to mass action. This process of complexion and readsorption is repeated many times causing the rare earths in effect to flow down the column but at a rate much lower than the flow rate of the eluent. In addition, the complexing action and adsorption equilibria are different for ions of different basicity, thus causing ionic bands to move down the cclumn at different rates, those with the highest atomic number moving at a faster rate and hence being eluted first.[5] To separate a group of rare earths then, the question is simply that of magnifying the differences in adsorption and complexion by use of several variables, chiefly; type and concentration of complexing agent, pH of eluent, dimensions of the column, and flow rate.

---

[5] Tompkins, E.R., Khym, J.X., Cohn, W.E., J.Am.Chem. Soc., 69, 2769 (1947)

CHAPTER III

EXPERIMENTAL

Apparatus

The apparatus for the actual column runs consisted essentially of a large pyrex tube approximately 47 mm inside diameter and 150 cm long having a coarse porosity fritted glass plate sealed into the bottom end. (Figure 2) A Dowex 50 resin bed was built up over the fritted plate to a depth of 120 cm. in the washed ammonium form of resin (the actual depth of bed varied from 118-120 cm during the runs -- shrinking as rare earths were adsorbed.) A constant head tank and a turntable which was actuated by a timer for automatic collection of fractions completed the column unit. The flow rate of effluent was controlled by a pinch clamp on the exit tube from the column proper and the rate of influent was dependent upon the effluent since the top of the column was closed by a rubber stopper. In addition to the column, a Beckman Model G glass electrode pH meter and a Beckman Model DU quartz spectrophotometer were used for analysis. The details of column operation, conditioning of the resin, and of the methods of analysis are give in Appendix I.

Materials

In order that the results of the proposed experiments might be compared with the results of those made previously, it was desirable that a starting mixture of essentially the

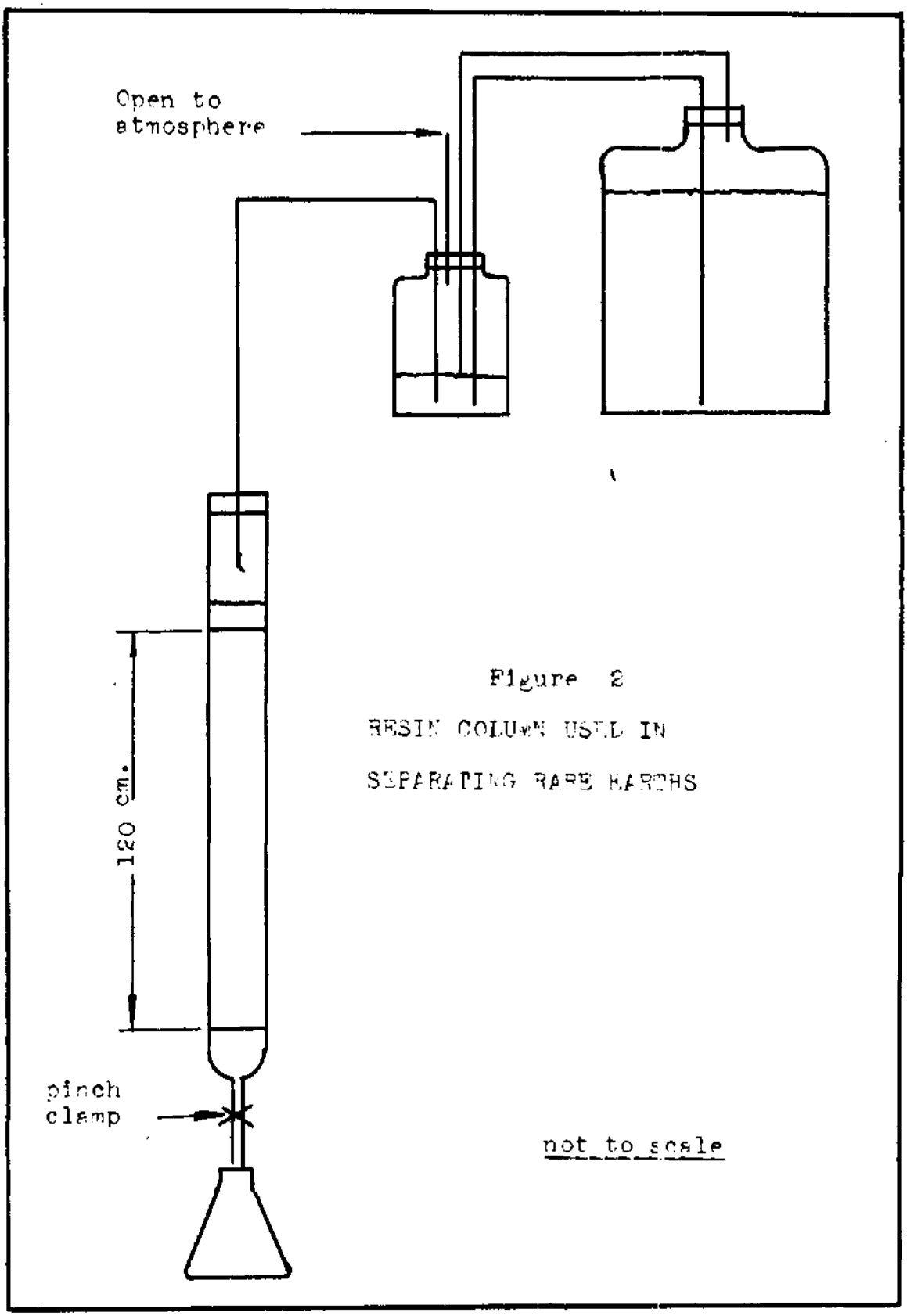


Figure 2

RESIN COLUMN USED IN

SEPARATING RARE EARTHS

not to scale

same composition as that used previously be obtained. Since none of the original mixture of oxides was still on hand, it was necessary to prepare the desired mixture from a quantity of "praseodymium ammonium nitrate" (actually a mixture of neodymium, praseodymium, lanthanum, and cerium ammonium nitrates) purchased from Lindsay Light and Chemical Company, West Chicago, Illinois. These nitrates were converted to the oxide form and the composition adjusted to that desired, utilizing some high purity laboratory stocks of praseodymium oxide which contained only a few per cent of neodymium oxide. The details of this operation are given in Appendix I. The final mixture of rare earths was kept in chloride solution of known concentration before adsorption as a convenience in handling. The final solution was analyzed and its composition found to be equivalent to that of an oxide containing 45.1% Pr_6O_{11}, 12.0% Nd_2O_3, 38.2% La_2O_3, and 4.7% CeO_2. The analysis of neodymium and praseodymium was performed spectrophotometrically; the percentage of ceric oxide was determined from Run 31 in which complete separation of this oxide was obtained; and the percentage of lanthanum oxide by difference. It may be noted at this point that the ceric oxide present represented an unexpected complicating factor in these experiments.

The eluent solution was made up by dissolving 900 gms of citric acid monohydrate and 18 gms phenol in 18 liters of distilled water to give approximately a 5% solution of citric

acid. First the citric acid and phenol were dissolved in the water, the solution made up to the desired volume, and then the pH was adjusted to the desired value by the addition of concentrated ammonium hydroxide. The function of the phenol was to prevent mold formation in the column. Spedding[1] using amberlite resins has found that o.1% of phenol is sufficient to prevent this growth and that up to 1.0% may be added without effect upon the shape or size of the elution bands. Further details concerning the making up of the eluent are presented in Appendix I.

Column Operation

A column run was started by neutralizing the adsorbate solution to as high a pH as was easily obtainable without precipitating rare earth hydroxides ---usually pH ≐ 2.0. This adsorbate solution at a concentration equivalent to approximately 30 grams of oxide per liter was then poured onto the column and the column washed with a liter of water. In general, the flow rate at which the loading was done was 20 ml. per minute (or 1.1-1.2 ml. per sq. cm. per minute). Experiments in progress by Roberts[2] in this Laboratory have indicated that adsorption of lanthanum under these conditions occurs in such a manner that a column length of approximately

---

[1]Spedding, F.H., et al., J Am. Chem. Soc., 69, 2812, (1947).

[2]Roberts, J.T.,Jr., unpublished work, Georgia Institute of Technology.

21 cm. (containing about one equivalent of resin) is required per equivalent of rare earth in the adsorbate solution. The fractions collected during loading and during washing have been designated fractions A and B, respectively, in the tabulated data concerning the column runs. At the completion of the washing, eluent of desired pH was introduced at the top of the column, the flow rate adjusted, and the run was under way. One hour fractions (about one liter per fraction) were taken except for the period when both neodymium and praseodymium were being eluted together, during which time half hour fractions were taken. As the fractions were collected, the volume, mean pH, and color of each was noted and then saturated oxalic acid solution added to precipitate the rare earths. The optical densities of the citrate solutions were checked at intervals by means of the spectrophotometer as a control device only, since concentrations were too low to give an accurate analysis. This device was particularly valuable in determining the overlap region. When the end point of the praseodymium elution curve was reached, as indicated by no precipitate upon the addition of oxalic acid, several additional fractions were taken to insure that all the praseodymium was off the column and then the pH of eluent was increased to remove the cerium and lanthanum which had remained on the column undisturbed by the low pH eluent. The location of the cerium depended upon the loading and pH as shown in the summary of column runs (Table I).

The oxalate precipitates were filtered, the filter paper ashed, ignited in a muffle furnace at 850° C. to convert the oxalates to the oxides, and the oxides weighed. Selected samples were taken from the fractions in the neodymium-praseodymium overlap region and analyzed spectrophotometrically.

CHAPTER IV

DISCUSSION OF RESULTS

As previously indicated, the experimental work consisted of preliminary preparations followed by six column runs which are summarized in Table I. The preliminary work has been discussed generally in former section and in detail in Appendix I. The elution curves of the six runs are of interest principally for comparative purposes and so, while the neodymium and praseodymium elution curves of all the runs are presented in Figures 7, 8, and 9, only one complete elution curve (Figure 3) has been included as a unit. It may be observed that the order of elution followed the order of decreasing atomic number, i.e., the neodymium, first, followed by praseodymium, cerium, and lanthanum in that sequence. The pH of the effluent has been plotted as well and it may be seen that as the concentration of rare earths increases in the effluent, the pH decreases and reaches minimum points corresponding to the various peaks. A consideration of the pH curve will also indicate another very important part of the separation process. That is, the pH of the eluent was increased to elute the lanthanum. On Run 31, this increase was accomplished in two steps, thus allowing the cerium to be removed at pH 3.20 before raising the eluent pH still further to remove the lanthanum.

TABLE I

SUMMARY OF COLUMN RUNS

Run #	pH *	Loading	Analysis of adsorbate	Gms of Nd_2O_3 starting oxide	Elution of Cerium
27	3.12	29.99 gms	45.1% Pr_2O_{11} 12.0% Nd_2O_3 38.2% La_2O_3 4.7% CeO_2	3.60	with tail of praseodymium
28	3.12	15.00 gms	as in Run 27	1.80	with lanthanum fractions
30	3.00	29.99 gms	As in Run 27	3.60	with lanthanum fractions
31	3.00	15.00 gms	As in Run 27	1.80	As a separate peak eluted at pH 3.20
33	3.12	30.00 gms	12% Nd_2O_3 88% La_2O_3	3.60	
34	3.12	3.60 gms	100% Nd_2O_3	3.60	

* For elution of neodymium and praseodymium fractions. All runs were made on 118-120 cm Dowex 50 ammonium form resin using 5% citric acid eluent solution with flow rate of approximately 1.1-1.2 ml. per cm^2 per minute.

FIGURE 3

CHARACTERISTIC ELUTION CURVE

Run 27

30 gm. loading

45.1% Pr_6O_{11}

12.0% Nd_2O_3

38.2% La_2O_3

4.7% CeO_2

pH of eluent = 3.12

pH of effluent (x--x)

gms. R. E. Oxide/liter (0--0)

pH of eluent was 3.12 for first 50 liters, 3.92 thereafter

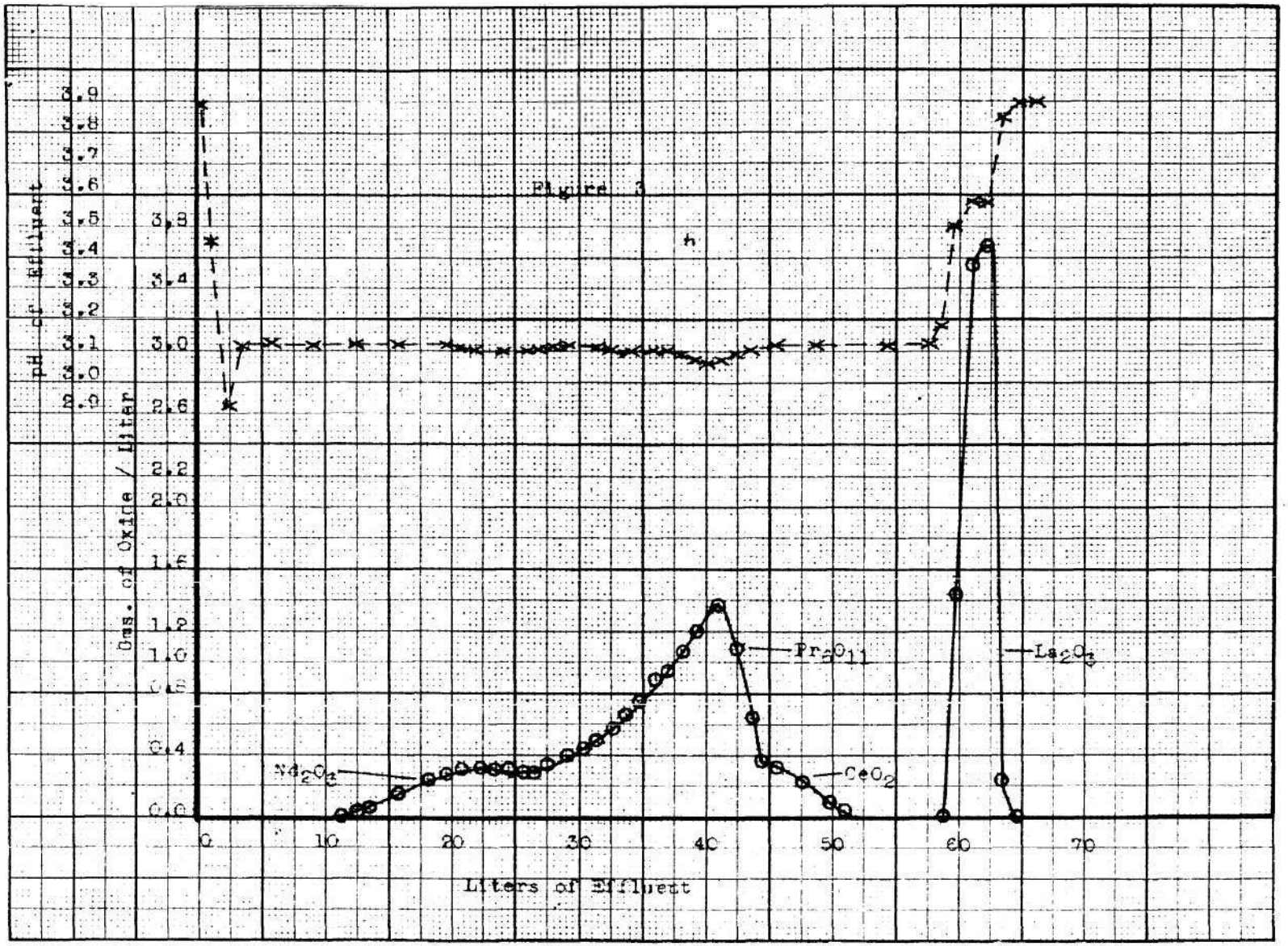


Figure 3
h
pH of Effluent
Gms. of Oxide / Liter
Liters of Effluent
Nd_2O_3
Pr_6O_{11}
CeO_2
La_2O_3
0
10
20
30
40
50
60
70
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
3.8
3.4
3.0
2.6
2.2
2.0
1.6
1.2
1.0
0.8
0.4
0.0

The elution curves for the other runs were similar in character (see Figures 7, 8 and 9) and data for their construction is presented in Appendix II along with analyses made, and material balances for each of the rare earths present in the run. It may be noted that the recovery varied between 95-100% based on the total oxide in the starting mixture and that the percentage recovery of each of the components is in line with this total, indicating that no great discrepancies in analysis or location of components were made. Thus, it is believed that the elution curves of the components are essentially correct and may be used independently of the total elution curves.

A consideration of Run 27, however, revealed several seeming irregularities;

1. The percentage recovery of neodymium oxide was 1.3% greater than 100. This is believed to have been due principally to impurities which were on the column before the run was started, and which came through with the first few fractions of rare earths. This conclusion was reached from the fact that a tan color exhibited by the oxide from the breakthrough fraction indicated that it, at least, was not 100% neodymium oxide. This indication was borne out by the analysis of this fraction as only 89% neodymium oxide.

It is also possible that some praseodymium oxide was counted as neodymium, thus swelling the percentage recovery. However, the recovery of praseodymium oxide for the same run

is calculated as nearly 99% indicating that if this were the case, only a very small amount of the praseodymium oxide was so considered.

2. The breakthrough in Run 27 came within a liter of the volume of effluent at which breakthrough was obtained on the shorter column (Run 29 by LaFond). This is equivalent to saying that in one case the neodymium band traveled through 120 cm. of resin in the same amount of time as was required for it to travel through 73 cm. of resin under conditions believed to be the same, which is of course, unreasonable. A later run (Run 33) on the longer column with the same total loading, containing the same amount of neodymium as Run 27, and at pH 3.12, gave breakthrough at about 15 liters of effluent which seemed more reasonable. Further, Run 34 with the same amount of neodymium and at pH 3.12 broke through after about 15.5 liters of effluent. It is true that the latter run had a smaller loaded length of column giving a greater free length, but this difference is proportionately a very small one. It would therefore seem reasonable to believe that Run 27 should not have exhibited breakthrough until about the 15th liter of effluent. A possible reason for the early breakthrough will be considered after the next irregularity is pointed out.

3. A comparison of the elution curves of Run 27 and Run 29 (Figure 4) showed that, while the distance between the neodymium and praseodymium peaks was greater for the run on

FIGURE 4

EFFECT OF COLUMN LENGTH

Run 27 (o--o)

120 cm. column

Run 29 (x --x)

75 cm. column

Both

Loading - 30 gms.

45.1% Pr_6O_{11}

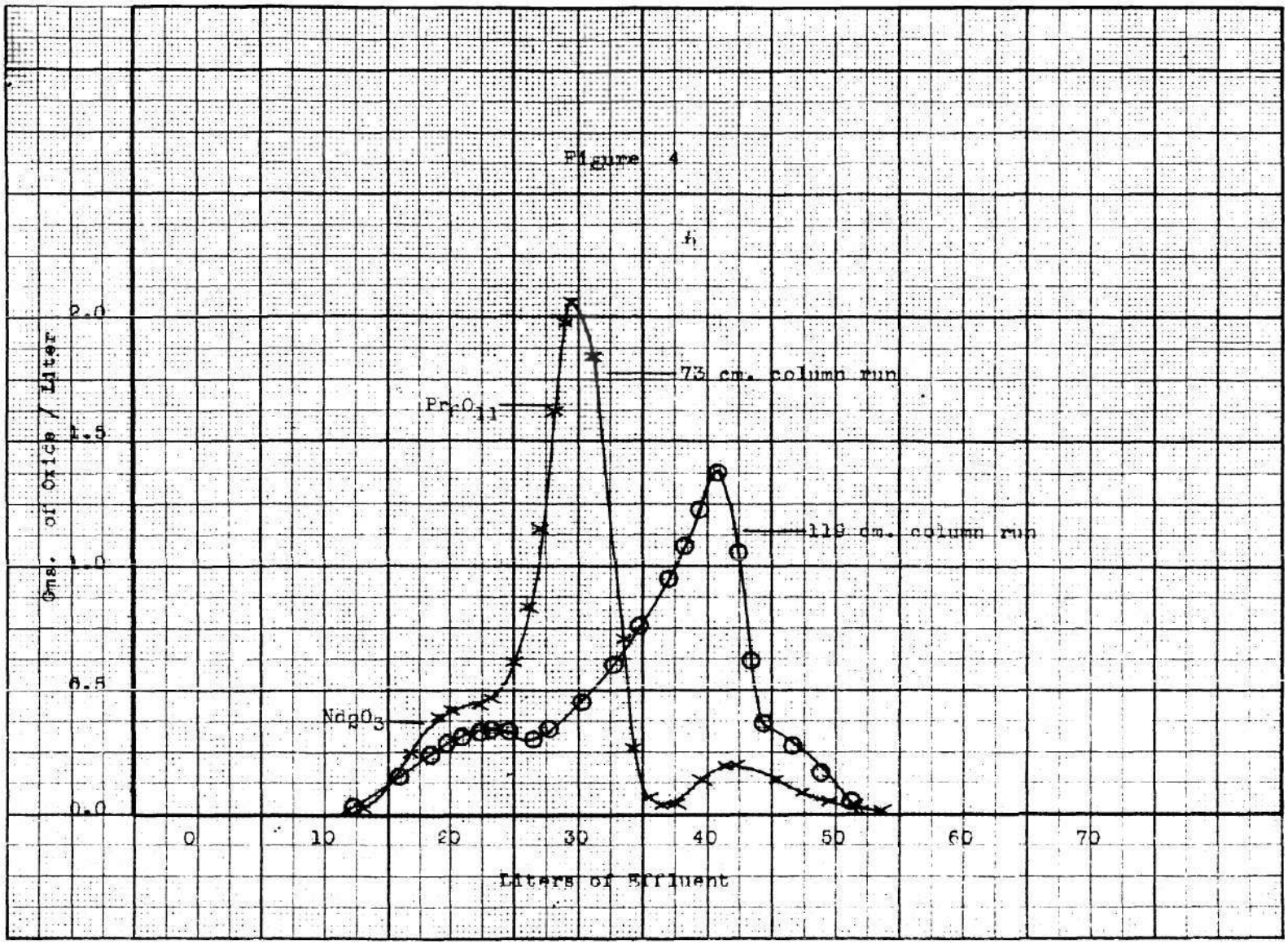
12.0% Nd_2O_3

38.2% La_2O_3

4.7% CeO_2

pH of eluent of 3.12

Figure 4


Gms. of Oxide / Liter
2.0
1.5
1.0
0.5
0.0
Pr_6O_{11}
Nd_2O_3
73 cm. column run
119 cm. column run
0
10
20
30
40
50
60
70
Liters of Effluent

the longer column, the cerium band was separated from the praseodymium by the shorter column and yet was nearly under the praseodymium peak in the long column run. This was directly contradictory to what had been expected as will be explained when the effect of column length is considered.

One possible explanation of these latter two anomalies is that the pH of the eluent used for Run 27 may have been a few hundredths of a pH unit higher than the set value of 3.12. First, consider that breakthrough was obtained in Run 28 (pH 3.12) with the 15th liter of effluent but not until the 46th liter in Run 31 (pH 3.00) . In other words, a known change of 0.12 pH units caused breakthrough to shift 31 liters --- a change of about $2\frac{1}{2}$ liters per 0.01 pH units. In the light of this fact, it is reasonable that an error of only 0.02 pH units, resulting in the pH of the eluent for Run 27 being actually 3.14, could have caused the breakthrough to come in the 10th liter instead of in the 15th liter as expected.

Furthermore, the elution of cerium was started with the 49th liter in Run 28 (pH 3.12) but had not started in Run 31 (pH 3.00) by the 99th liter at which time the pH was raised. This constituted a change of cerium band location of about 4 liters per 0.01 pH units. It seems quite possible, then, that an error of 0.02 pH units, resulting in the pH of eluent (Run 27) actually being 3.14, might cause the cerium band to be moved forward as compared to the short column run (Run 29) instead of increasing the peak separation as had been expected.

It is perhaps surprising at first glance that a small change in pH should have an effect upon the cerium band nearly twice as great as its effect upon the neodymium breakthrough. However, it is believed that this difference in behavior is due principally to the particular range of pH in which the effects were observed. In other words, at a different pH range, a smilar error in pH would still probably affect cerium elution more than it would neodymium elution but the difference in effect would not be so striking.

Flow rate

It was thought that the overhead tank arrangement (see Figure 2) was such that the eluent head would be controlled to within approximately one inch. Even so, a maximum variation in flow rate of about 10% was observed in Run 27 and a variation of about 30% in the succeeding runs. The average flow rate for any particular run was, however, between 0.99 and 1.09 ml./min.cm^2 Although, Spedding[1] has indicated that flow rate can affect elution, his result was obtained with changes of flow rate on the order of 100-400% and it is believed that the variation of flow rate had little or no effect upon the results of the experiments presented in thi s thesis.

---

[1]Spedding, et al., J. Am. Chem. Soc., 69, 2786(1947).

Acid front limitation

As pointed out earlier, when the effect of pH was studied on short (73 cm.) column, the neodymium elution curve exhibited an anomaly. As the pH was raised from 2.90 to 3.00 and thence to 3.12, the praseodymium elution curves tended to narrow the band and the peak grew higher progressively (Figure 1). However, while the neodymium elution curve changed in a similar manner for the change of pH from 2.90 to 3.00, on the additional change from 3.00 to 3.12, the neodymium elution curve became again lower and broader. It was thought at the time that this effect might possibly have been due to an excess of acid known to have been present in the adsorbate solution. Conceivably, the hydrogen ions were adsorbed onto the column below the rare earths and thus formed a boundary of low pH through which the neodymium band could not move. When this hydrogen band moves slower than the neodymium band, the neodymium tends to "pile up" behind the hydrogen and neodymium breakthrough cannot occur until shortly after the end of the acid band elution. This effect has been pointed out by other workers[2] and is discussed in detail by Tompkins, et al.,[3] being especially evident when acid

---

[2]Tompkins, E.R., Khym, J.X., and Cohn, W.E., J.Am.Chem. Soc., 69, 2769, (1947).

[3]Tompkins, E.R., Harris, D.H. and Khym, J.X., J.Am. Chem. Soc., 71, 2504 (1949).

form resins or high pH eluent solutions are used.

In order to avoid this effect in the present experiments an adsorbate solution wasused which had been neutralized with dilute ammonium hydroxide to as high a pH as was easily obtainable without precipitation of the rare earth hydroxides. (approximately pH 2.0) Run 29[4] essentially duplicated the former run (Run 24) except for the neutralization of the adsorbate and Run 27 was under the same conditions as Run 29 except for the use of a 120 cm. resin column for Run 27 as compared to 73 cm. for Run 29. When it was observed that the neodymium elution curves for Runs 27 and 29 did not materially differ from the one obtained in the previous experiment, i.e., Run 24, it was concluded that the anomaly was not due to acid front limitation.

Effect of pH

Walter[5] has examined the problem of adsorption of solutes treated in a manner similar to that employed in ion exchange. He assumed chemical equilibrium between adsorbed material and the solution, and was able to describe mathematically the distribution of adsorbed material for one or more components for the case of monovalent- monovalent adsorption; i.e., both the adsorbed and displaced ions were monovalent. He describes a band with a sharp front for K$>$ 1

---

[4]LaFond, F., unpublished work, Georgia Institute of Technology, April, 1950.

[5]Walter, J.E., J. Chem. Phys., 13, 229-234, (1945).

and a diffuse front for K < 1 where for the equilibrium reaction:

$$HR + M^{+} \rightleftharpoons MR + H^{+}$$

$$K = \frac{(\text{conc. of } M^{+} \text{ on the resin})\ (\text{conc. } H^{+} \text{ in soln.})}{(\text{Conc. of } H^{+} \text{on the resin})\ (\text{conc. } M^{+} \text{ in soln.})}$$

all values of concentrations being those at equilibrium. Further, he concludes that as the band is developed or passes down the column, a band with a sharp front boundary and diffuse rear boundary is formed for K > 1 and a band with sharp rear boundary and diffuse front is formed for K < 1. That is, the elution curves obtained would be shaped thus:

K > 1

K < 1

The mathematical expressions are derived for the monovalent-monovalent exchange as mentioned above but the author states that the conclusion should be applicable qualitatively to exchange of ions of higher valence as well.

If now the shape of the praseodymium curves (Figure 5) are examined for pH of 3.00 and of 3.12, for the runs on the longer column, the effect of change of pH is seen to be that of causing a marked change in the shape of the individual elution curves. If we may let K become a function representing the relative affinity of the adsorbing ion to that of the ion already on the resin, then the qualitative result may be stated that for K > 1 a curve is obtained with a sharp front

FIGURE 5

EFFECT OF pH ON SHAPE OF PRASEODYMIUM

Elution Curves

Run 27 (X)

pH 3.12

Run 30 (0)

pH 3.00

Both:

120 cm. column

30 gm. loading

45.1% Pr_6O_{11}

12.0% Nd_2O_3

38.2% La_2O_3

4.7% CeO_2

FIGURE 5

EFFECT OF pH ON SHAPE OF PRASEODYMIUM

Elution Curves

Run 27 (X)

pH 3.12

Run 30 (0)

pH 3.00

Both:

120 cm. column

30 gm. loading

45.1% Pr_6O_{11}

12.0% Nd_2O_3

38.2% La_2O_3

4.7% CeO_2

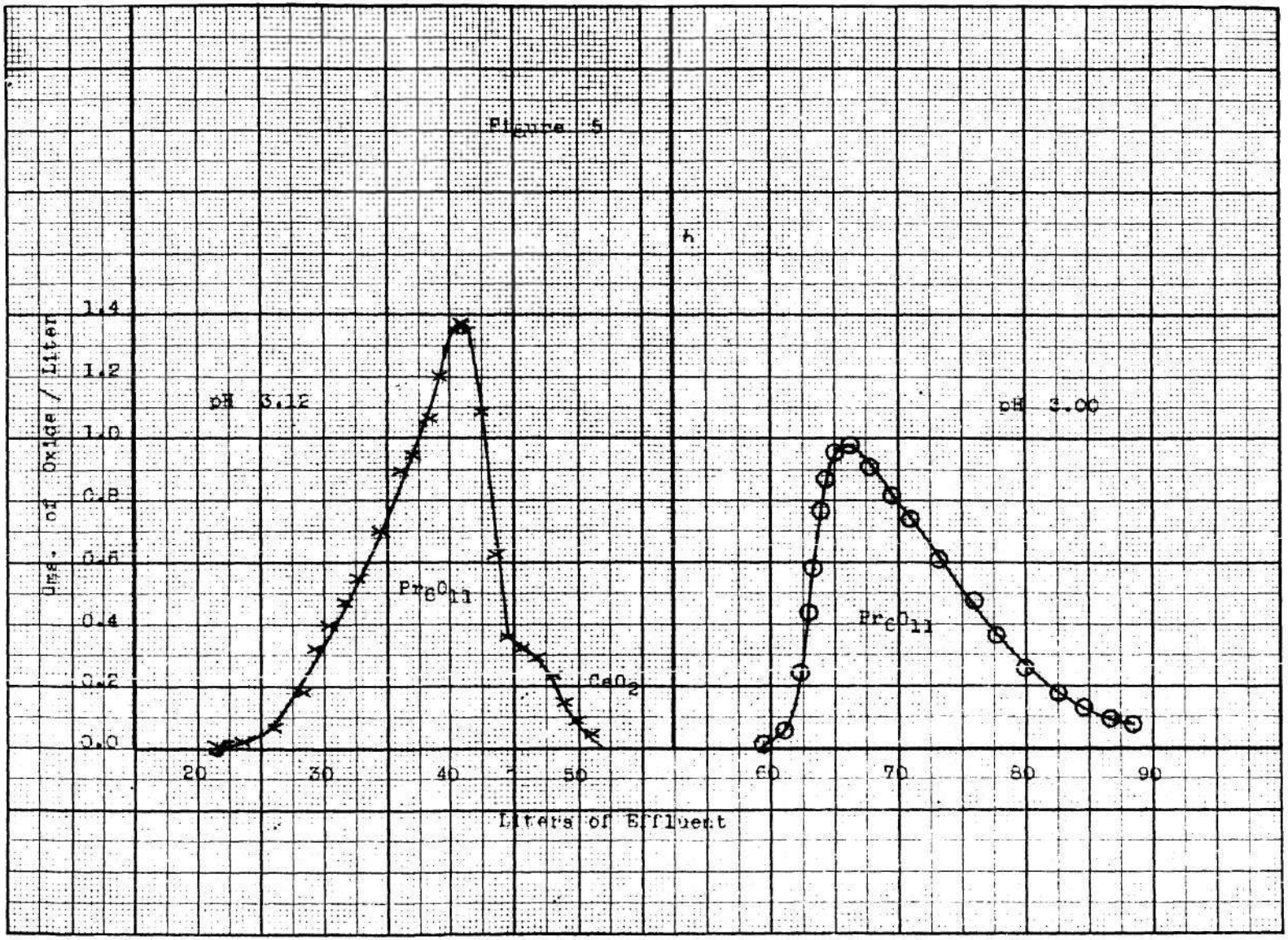
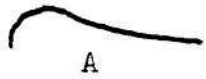
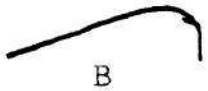


Figure 5
pH 3.12
pH 3.00
PrcO_{11}
PrcO_{11}
CeO_2
Gms. of Oxide / Liter
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
20
30
40
50
60
70
80
90
Liters of Effluent

boundary and a diffuse rear boundary, and for K < 1 a curve is obtained with a diffuse front boundary and a sharp rear. Applied to the praseodymium curves we obtain:

pH 3.00  K > 1

A

pH 3.12  K < 1

B

It would seem, reasonable to assume that at some intermediate pH a symmetrical elution curve would be obtained for which K = 1. Thus, in a manner of speaking, it may be stated that the effect of a pH change is to change the affinity of the rare earth ions for the resin due to the effect of both changing the equilibrium concentration of the citrate complexing ion and changing the ammonium ion concentration. Further, at some pH, specific for each rare earth ion for a given resin, the affinity will be such that K = 1 giving a symmetrical elution curve. For values of pH above this value, the curve will be longer on the leading edge and for values of pH below the specific, the curve will be longer on the trailing edge.

Inasmuch as the curves for neodymium obtained on the longer column runs did not seem to show this effect to any great degree, (Figure 6) the question was raised as to whether at pH 3.12 the neodymium elution curve was skew or dymmetrical since the above theory would suggest that one might expect this curve to be shaped as curve B above while the elution curve appeared nearly symmetrical. It was decided

FIGURE 6

EFFECT OF pH OF ELUENT ON SHAPE

OF NEODYMIUM ELUTION CURVES

Run 27

pH 3.12 (X)

Run 30

pH 3.00 (0)

BOTH:

120 cm resin column

30 gm. Total loading

45.1% Pr_6O_{11}

12.0% Nd_2O_3

38.2% La_2O_3

4.7% CeO_2

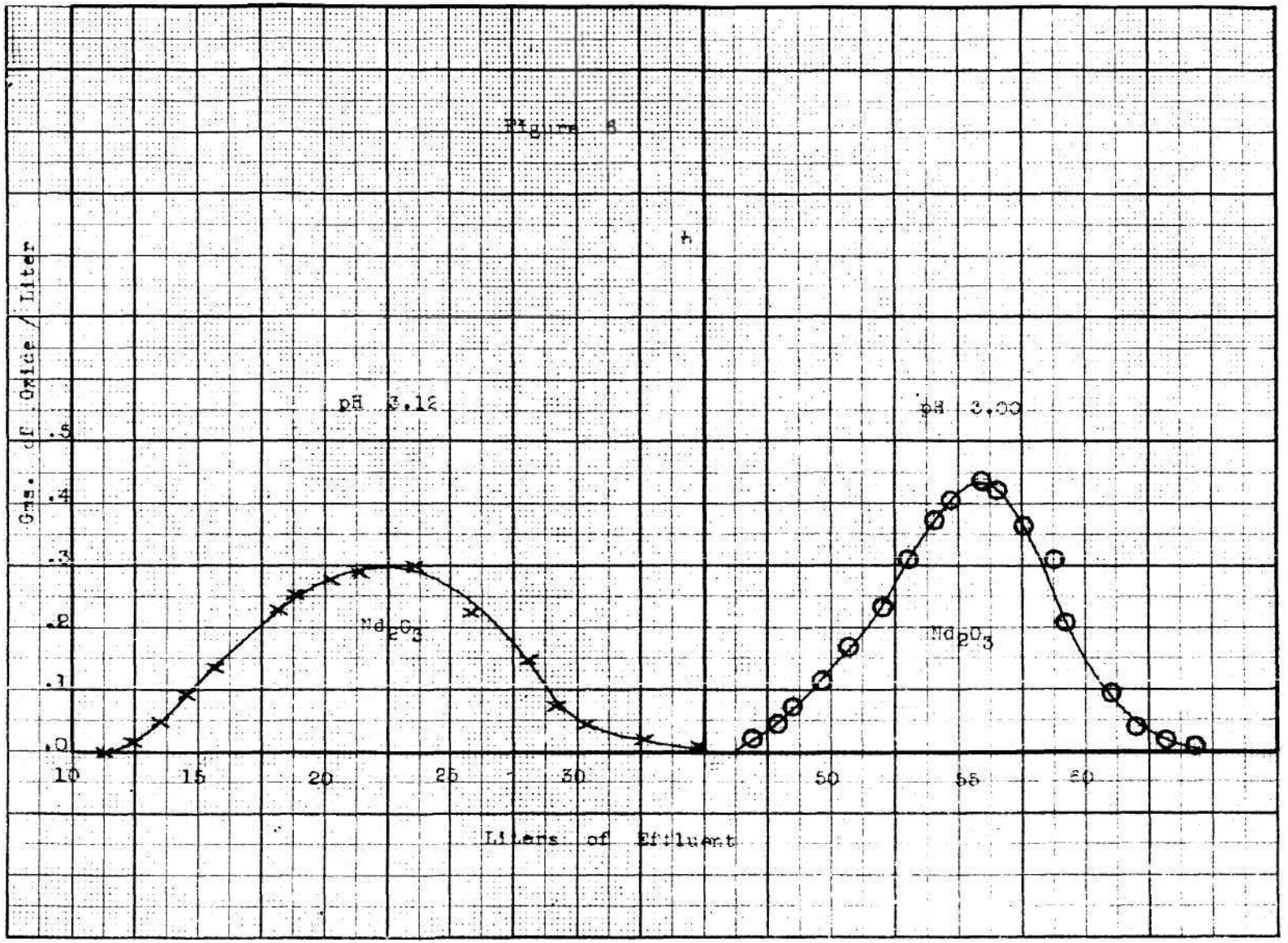


Figure 8
Gms. of Oxide / Liter
.5
.4
.3
.2
.1
.0
pH 3.12
pH 3.00
Nd_2O_3
Nd_2O_3
10
15
20
25
30
50
55
60
Liters of Effluent

to make one run loading with just the amount of neodymium that was contained in the former runs and another, loading with the same amount of neodymium but making the total loading up to 30 gms. with lanthanum oxide. It was hoped that these runs (33 and 34) would show the effect of the neodymium curve at pH 3.12 unaffected by the presence of other elements and also the effect of lanthanum, if any. As shown in Figure 7, the curve at this pH is indeed longer on the front than on the rear as theory had predicted. The presence of lanthanum seemed to have had no effect at all upon the shape of the curve. The slightly earlier breakthrough in run 33 may have been due to the larger total load giving a shorter effective column length or it may have been due to other factors varying within the limits of experimental error. The presence of praseodymium, however, seems to have caused the neodymium elution curve to tail out under the praseodymium elution curve to some extent. (See Run 27, Figure 7). When the curves obtained by varying pH for the earlier experiments are reexamined, (Figure 1) the effects explained above are evident although obscured to some extent by the scale required to place all three curves on the same plot, resulting in the effect not being particularly noticeable until exaggerated by the longer column. It may be noted that the shapes exhibited by the earlier curves (Figure 1) are as follows:

pH	Nd	Pr
3.12	B	B
3.00	B	A
2.90	A	A

FIGURE 7

NEODYMIUM ELUTION CURVES

SHOWING EFFECT OF PRESENCE OF

OF OTHER RARE EARTHS

Run 27 - (⊡—⊡) Nd_2O_3, Pr_6O_{11} and La_2O_3 in adsorbate (30 gms total loading)

Run 33 (X--X) Nd_2O_3 and La_2O_3 in adsorbate (30 gms total loading)

Run 34 (0--0) Nd_2O_3 only in adsorbate (3.6 gms loading)

All runs:

120 cm column

pH of eluent = 3.12

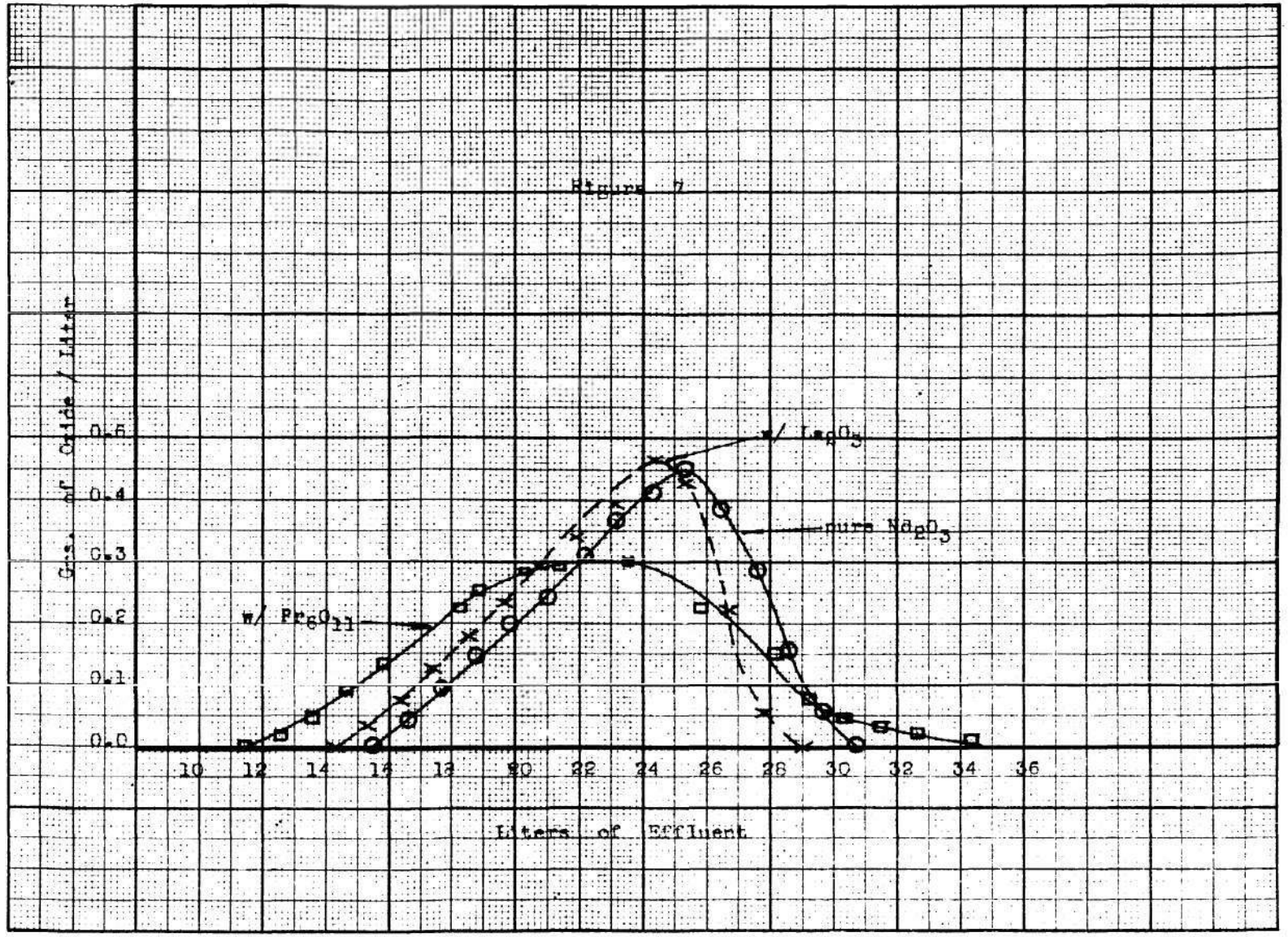


Figure 7
Grs. of Oxide / Liter
0.6
0.4
0.3
0.2
0.1
0.0
w/ La_2O_3
pure Nd_2O_3
w/ Pr_6O_{11}
10
12
14
16
18
20
22
24
26
28
30
32
34
36
Liters of Effluent

The effect of pH on the movement of the cerium band has already been noted. It seems to have a surprisingly large effect when varied over the small range between pH 3.00 and 3.12 but perhaps this is not unreasonable when it is considered that essentially the same effect has been observed for lanthanum which seems to move infinitesimally slowly even at pH 3.20 but very rapidly at pH 3.90 (see Run 31).

Effect of Column Length

As discussed in a previous section on general theoretical background, the use of ion exchange to separate the components in a mixture of rare earths is dependent upon differences in their respective exchange equilibrium constants and on differences in the dissociation equilibrium constants of the complexes of the various rare earths. These differences cause the various components to move down the resin column in bands having different rates of movement for different components. Since they are moving at different rates, it would seem that the further they travel before elution, or the longer the free length of column, the greater should be the separation of the bands, and hence, of the components. This effect was, indeed, noted by Spedding[6], for this reason the runs for this thesis were all made on a column considerably longer than the column used for previous experiments in this

---

[6] Spedding, et al., J. Am. Chem. Soc., 69, 2777 and 2786, (1947).

laboratory. The greater separation of the neodymium and praseodymium peaks given by the longer column as compared to that obtained on the short column[7] is very noticeable (Figure 4). However, as pointed out by Harris, Tompkins, and Khym[8], a widening of the elution bands may be expected with increasing column length according to either the mass transfer[9] or the plate[10] theory of chromatography. This effect was indeed noted in a spreading of the bands (i.e., a decrease in slope of the leading and trailing edges.) The net result of these two effects was that no appreciably better separation was obtained for this particular mixture of oxides by lengthening the column alone. This result may be seen by a comparison of a previous run made at this Laboratory (Run 24) and LaFond's Run 29 (both on a 73 cm. column and under similar conditions of pH of eluent, composition of adsorbate, type of resin bed, and flow rate) with Run 27 made under similar conditions except for the use of a longer resin column (See Table IIa). A comparison of another previous run (Run 23) at pH 3.00 with Run 30 (Table IIa) (the long column run at 30 gm. loading and pH 3.00) would perhaps seem to indicate

---

[7]Short column run used for comparison (Run 29) made by LaFond, F., Georgia Institute of Technology, April 1950.

[8]Tompkins, E.R., Harris, D.H., and Khym, J.X., J. Am. Chem. Soc., 71, 2504 (1949)

[9]Boyd, G.E., Myers, L.S., Jr., and Adamson, A.W., J. Am. Chem. Soc., 69, 2849 (1947)

[10]Mayer, S.W., and Tompkins, E.R., J. Am. Chem. Soc., 69, 2769 (1947)

TABLE IIa

PURITY OF RECOVERED OXIDES [a]

Run No.	pH of eluent	Total column loading (gms.)	column length (cm.)	Neodymium Oxide: Percent of oxide recovered as oxide having purity greater than 90%	95%	98%	Praseodymium Oxide: Percent of oxide recovered as oxide having purity greater than 90%	95%	98%
24	3.12	30	73	73[b] (7)	73 (7)	46 (5)	94 (9)	88[c] (8)	88 (8)
27	3.12	30	120	72 (16)	57 (14)	42 (9)	90 (30)	85 (28)	83 (27)
29	3.12	30	73	62 (13)	55 (12)	49 (11)	87 (17)	79 (15)	74 (14)
23	3.00	30	73	82[b] (5)	82[c] (5)	82 (5)	94[c] (26)	94 (26)	87 (25)
30	3.00	30	120	93[b] (22)	93 (22)	85 (20)	102 (43)	98 (42)	94 (41)

a For sample calculations see Table XX

b Indicates that no fraction was obtained of purity greater than 90% but less than 95%

c Indicates that no fraction was obtained of purity greater than 95% but less than 100%

Note: Numbers in parentheses indicate the number of fractions summed to obtain the weight of oxide having the designated purity.

slightly better separation on the longer column. However, the increase is so slight as to be influenced by size of fractions taken and number of fractions considered in setting the limits of purity as well as by other experimental limitations on reproducibility so that no real conclusion could be drawn as to whether or not separation was affected by increasing the column length. Inasmuch as lengthening the column increases the length of the run and the amount of eluent solution required, the practical conclusion may be drawn that for this particular separation, a column shorter than 120 cm. should be used.

Effect of loading

It was expected that if a smaller loading was used under a given set of conditions, narrower bands of the individual components would be formed upon original adsorption. In fact, Spedding[11] found that the actual space required for the rare earths upon loading was directly proportional to the weight of the sample. Thus, if the loading was reduced by one half, the column length would be increased but not nearly in proportion to the reduction in band size and the net effect was expected to be that of aiding separation. Indeed, a comparison of the elution curves of Run 27 (30 gms.) with those of Run 28 (15 gms) (Figure 8) both at pH 3.12 would seem to indicate that better separation of the components is

---

[11]Spedding, et al., J.Am. Chem. Soc., 69, 2786,(1947)

FIGURE 8

EFFECT OF LOADING

Run 27 (Q)

30 gm. loading

Run 28 (X)

15 gm. loading

Both
pH of eluent - 3.12

Composition of adsorbate:

45.1% Pr_6O_{11}

12.0% Nd_2O_3

38.2% La_2O_3

4.7% CeO_2

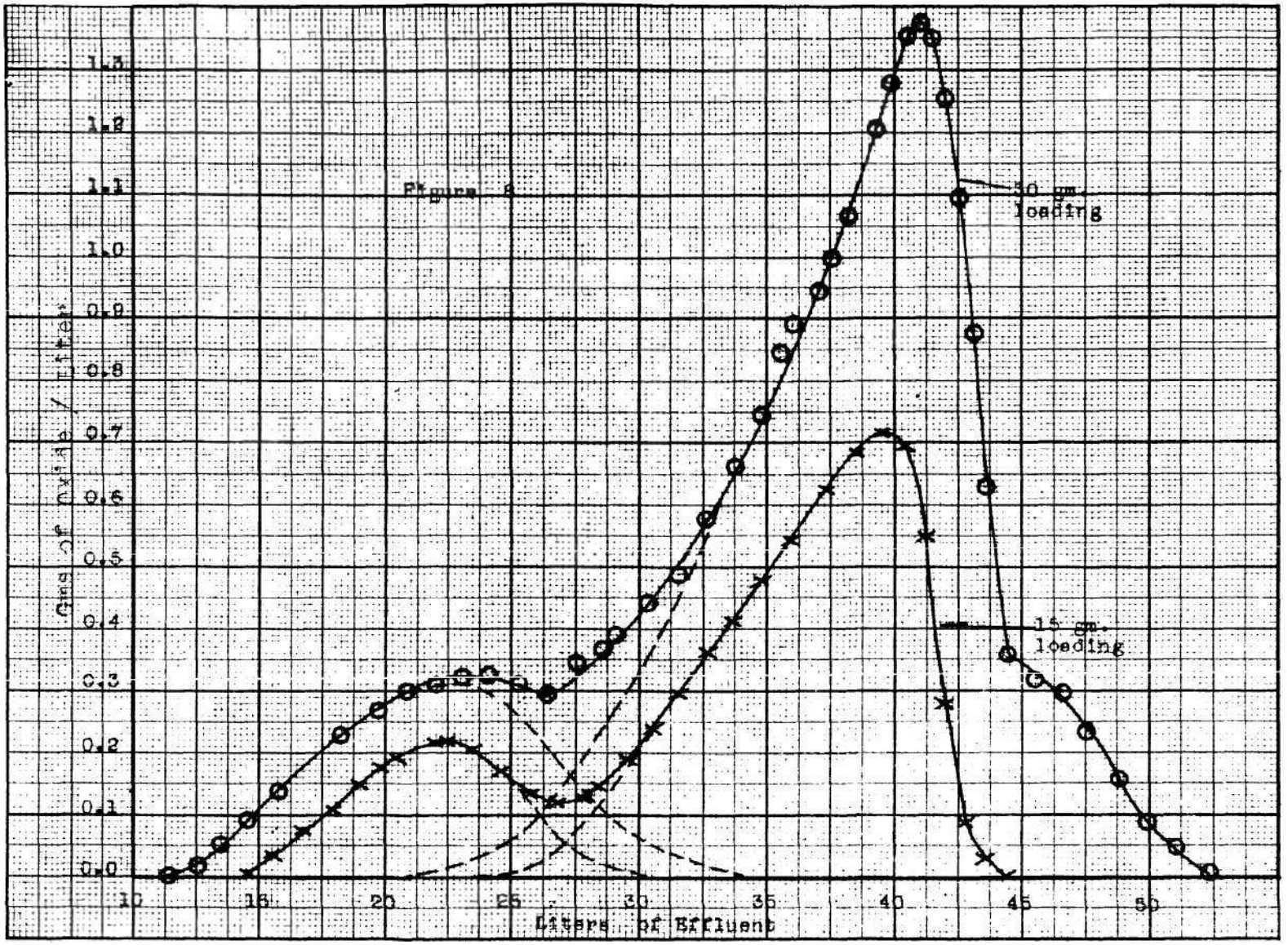


Figure 8
30 gm. loading
15 gm. loading
Gms of oxine / liter
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
10
15
20
25
30
35
40
45
50
Liters of Effluent

obtained since a decrease in the size of the overlap region may be observed with decreased loading. A comparison of the tabulated percentage recovery of oxides of various purity for these two runs (Table IIb) would tend to bear this out. In addition, a comparison of the elution curves of Run 30 (30 gms.) with Run 31 (15 gms) both at pH 3.00 would seem by the same criterion of comparative sizes of overlap regions to indicate an improvement in separation. (Figure 9) However, a comparison of percentage recoveries of various purity for these latter two runs (Table IIb) does not show any appreciable difference in separation. It may be simply that with the separation of components already so greatly enhanced by the lower pH, any small improvement due to reduced loading is covered by variation of other conditions within the limits of experimental error, as well as by factors such as size of fractions collected and the possible large effect of one or two fractions on the particular percentage purity under consideration.

A consideration of the two comparison curves (Figure 8 and 9) together raised a question as to the effect of loading upon the location of the praseodymium peak. In one case (Figure 8) at pH 3.12 the peak is shifted toward the earlier part of the run, and in the other (Figure 9) the peak is shifted away from the earlier part of the run. In both cases, however, the peak is shifted toward the diffuse

TABLE IIb

PURITY OF RECOVERED OXIDES a

Run No.	pH of eluent	Total column loading (gms.)	column length (cm.)	Neodymium Oxide: Percent of oxide recovered as oxide having purity greater than 90%	Neodymium Oxide: 95%	Neodymium Oxide: 98%	Praseodymium Oxide: Percent of oxide recovered as oxide having purity greater than 90%	Praseodymium Oxide: 95%	Praseodymium Oxide: 98%
27	3.12	30	120	72 (16)	57 (14)	42 (9)	90 (30)	85 (28)	83 (27)
28	3.12	15	120	88 (15)	83 (14)	72 (12)	96 (22)	93c(20)	93 (20)
30	3.00	30	120	93b(22)	93 (22)	85 (20)	102 (43)	98 (42)	94 (41)
31	3.00	15	120	96 (23)	92c(21)	92 (21)	99 (27)	97 (25)	95 (24)

a. For sample calculations see Table XX.

b Indicates that no fraction was obtained of purity greater than 90% but less than 95%.

c Indicates that no fraction was obtained of purity greater than 95% but less than 100%.

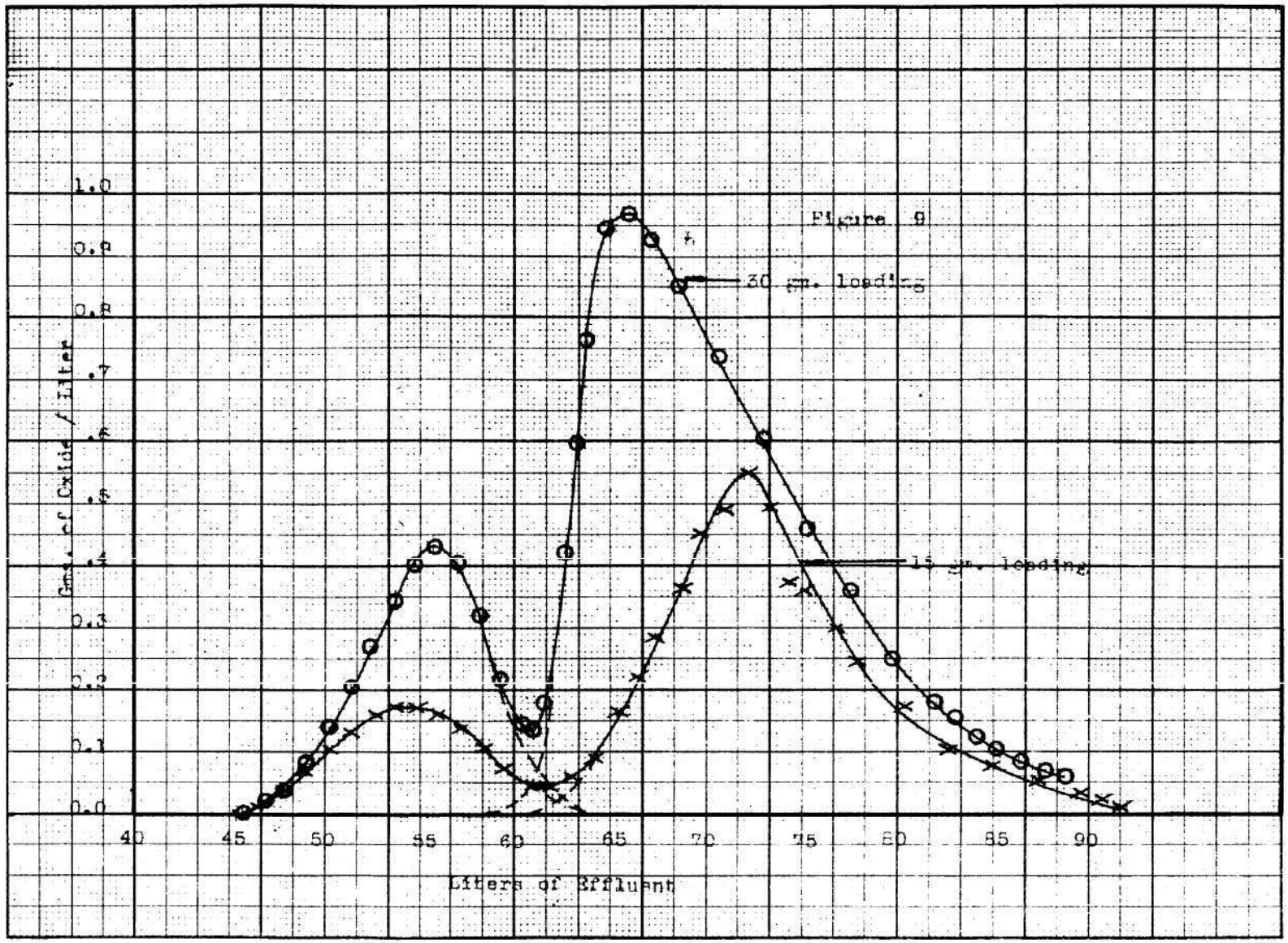


Figure 9
30 gm. loading
15 gm. loading
Gms. of Oxide / Liter
1.0
0.9
0.8
.7
.6
.5
.4
0.3
0.2
0.1
0.0
40
45
50
55
60
65
70
75
80
85
90
Liters of Effluent

side of the curve rather than toward the sharper edge. It may be that this effect is coincidence and caused by slight changes in other variables than loading. On the other hand, it may be that further experimentation could establish a trend with increasing or decreasing loading. In any event, this question must remain unanswered for the present.

FIGURE 9

EFFECT OF LOADING

Run 30 (O---O)

30 gm. loading

Run 31 (X---X)

15 gm. loading

Both

pH of eluent - 3.00

120 cm. Dowex 50 column

Adsorbate: 45.1% Pr_6O_{11}

12.0% Nd_2O_3

38.2% La_2O_3

4.7% CeO_2

CHAPTER V

CONCLUSIONS

Some studies have been made on the effect of pH of eluent, column length, and loading upon the separation of praseodymium and neodymium from a mixture of oxides containing approximately 12.0% Nd_2O_3, 45.1% Pr_6O_{11}, 4.7% CeO_2, and 38.2% La_2O_3. The greatest effect was found by variation of the pH of the eluent. This effect was such that it was definitely indicated that for the two ions studied in particular, and probably for any two ions in general, there is an optimum pH for maximum separation. This pH is such that the affinity of one ion for the resin is greater than that of the ion to be displaced and such that the affinity of the second ion is less than that of the ion to be displaced. For example, in the separation of neodymium and praseodymium using ammonium form resin, the affinity of neodymium for the resin should be less than that of the ammonium, and the affinity of the praseodymium for the resin should be greater than that of the ammonium. For the particular separation studied, this pH is believed to be between pH 3.00 and 3.12, perhaps closer to 3.00.

An increase in column length tended to increase the distance between peaks in the elution curve but to widen the bands at the same time so that no appreciable effect on com-

ponent separation was noted from the increase in column length used in these experiments. Since the longer column did, however, cause the length of the run to be increased and the time consumed to be greater, it is believed that the use of the shorter column is more practical for this particular separation.

A decrease in loading at a pH away from the optimum tended to give better separation of the components. At a pH near the optimum, however, no appreciable effect was noted as a result of lessening the load. It may well be that if better control of all other variables was obtained then a small effect might be found. An unexplained effect was noted upon the shape of the praseodymium curve and the location of that peak which would indicate that more experimental results are necessary to a full understanding of the effect of this variable.

BIBLIOGRAPHY

Bauman, W.C., and Eichorn, J., J. Am. Chem. Soc.,69,2830,(1947)

Boyd, G.E.,Myers, L.S., Jr., and Adamson, A.W., J. Am. Chem. Soc., 69, 2849, (1947)

Harris, D.H., and Tompkins, E.R., J. Am. Chem. Soc., 69 2792, (1947)

LaFond, F., unpublished work, Georgia Institute of Technology, (1950)

Mayer, S.W, and Tompkins, E.R., J. Am. Chem. Soc., 69 2866, (1947)

Nachod, F.C., Ion Exchange Theory and Applications, Academic Press, Inc., New York, N.Y. (1949)

Roberts, J. T., Jr., unpublished work, Georgia Institute of Technology, (1950).

Tompkins, E.R., Khym., J.X., and Cohn, W.E., J. Am. Chem. Soc. 69, 2769 (1947).

Tompkins, E. R., Harris, D. H. and Khym, J. X., J. Am. Chem. Soc., 71 , 2504 (1949)

Spedding, F. H., Voigt, A.F., Gladrow, E. M., Sleight, N.R., J. Am. Chem. Soc., 69, 2777, (1947)

Spedding, F. H., Voigt, A. F., Gladrow, E. M., Sleight, N.R., Powell, J.E., Wright, J. M., Butler, T.A., and Figard, P., J. Am. Chem. Soc., 69, 2786, (1947).

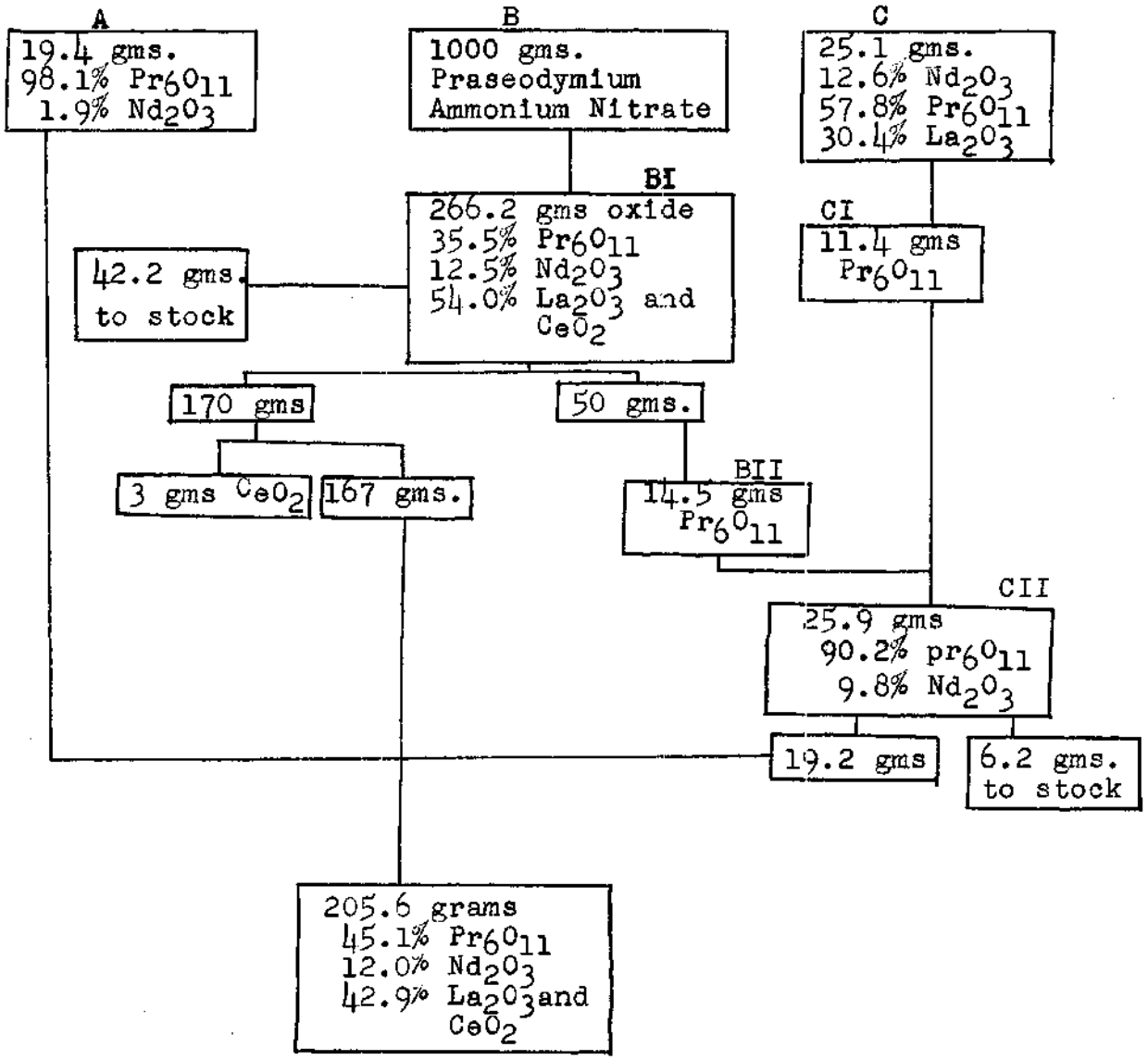
Spedding, F. H., Fulmer, E.I., Butler, T. A., Gladrow, E. M., Gobush, M., Porter, P. E., Powell, J.E., and Wright, J. M., J. Am. Chem. Soc., 69, 2812 (1947).

Walter, John E., J. Chem. Phys., 13, 229-234, (1945)

Ziegler, W.T., Blomeke, J.O., Roberts, J.T., Jr., Paper presented before Georgia Section - American Chemical Society, Meeting in Miniature, November 17, 1949.

APPENDIX I

Figure 10



APPENDIX I

Preparation of Adsorbate Solution.

To compare the proposed experiment with previous ones conducted in this laboratory, it was desirable to use a rare earth oxide mixture with approximately the same composition as that used for the previous experiments, i.e., approximately 10% Nd_2O_3 , 45% La_2O_3 , and 45% Pr_6O_{11}. As starting material there was available a quantity of praseodymium ammonium nitrate described by its manufacturer, Lindsay Light and Chemical Co. as about 30% oxide, containing 32% Pr_6O_{11}, 10% Nd_2O_3, 4% CeO_2, and 54% La_2O_3 with traces of other rare earth oxides; and some laboratory stocks of high purity praseodymium oxide containing a few percent of neodymium oxide. The manner in which the adsorbate solution was prepared may be most easily followed on Figure 10.

First, 1000 grams of praseodymium ammonium nitrate were dissolved in water and filtered to remove dirt and insoluble material. Then saturated oxalic acid solution was added to precipitate the rare earths as the oxalates. After filtering, the residue was ignited overnight at 850° C. The oxides thus formed were redissolved in 2N HCl and filtered in an attempt to remove as much of the CeO_2 as possible, CeO_2 being relatively insoluble in dilute HCl. This solution was neutralized with dilute ammonium hydroxide until the

rare earth hydroxides started to form, enough HCl was added to barely redissolve the hydroxides and then saturated oxalic acid solution added to again precipitate the rare earth oxalates. The residue, after filtration, was once again ignited in the muffle furnace overnight to yield 266.2 grams of oxide (BI) which was analyzed spectrophotmetrically as 33.5% Pr_6O_{11} and 12.5% Nd_2O_3.

When one batch of laboratory stock (C) was analyzed, it was found to contain 25.1 grams of oxide 12.6% Nd_2O_3 and 57.8% Pr_6O_{11} with the remaining 30.4% presumably being La_2O_3 To obtain purer Pr_6O_{11} for the formulation of the adsorbate solution, this mixture was fractionated by a column run over Dowex 50 resin which was used with citric acid eluent at pH 3.20. The praseodymium rich fraction (C I) weighed 11.4 grams. Since more relatively pure praseodymium oxide was needed, fifty grams of BI was fractionated similarly, yielding a praseodymium fraction, BII, of 14.5 grams. These two fractions (CI AND BII) were combined and the mixture (CII) analyzed as 25.9 grams oxide containing 90.2% Pr_6O_{11} and 9.8% Nd_2O_3.

One hundred seventy grams of BI were dissolved in about 3 M HCl and filtered to remove the CeO_2 which did not dissolve. Later developments indicated that at least a portion of the CeO_2 was soluble in the HCl and thus remained with the adsorbate. This filtrate was combined with 19.2 grams of CII and with the other batch of laboratory stock (A) consisting of 19.4 grams of oxide analyzing 98.1% Pr_6O_{11} and 1.9% Nd_2O_3 to give the adsorbate mixture of 205.6 grams of oxide

analyzed as 45.1% Pr_6O_{11} ; 12% Nd_2O_3; 38.2% La_2O_3 and 4.7% CeO_2.

Conditioning of the resin

The Dowex 50 resin for these experiments had been used for a number of previous runs and the impurities originally present such as iron, calcium, etc. had been removed at that time. The resin was screened in the air dry form and found to be approximately 11.7% between 35 and 50 mesh, 54.0% between 50 and 80 mesh, and 34.3% less than 80 mesh. The resin was then placed in a column and converted to the ammonium form by passing "five percent citric acid" solution adjusted to a pH of 3.9 with ammonium hydroxide, through the column. This process was continued until the pH of the effluent was equal to the pH of the influent. After the first run, the elution of lanthanum with eluent of pH 3.9 or greater accomplished the same purpose.

Loading the Column

The adsorbate solution was divided into quantities containing the required amount of rare earth chlorides for the various runs (2 quantities equivalent to 30 gms. total oxide and 2 equivalent to 15 gms. total oxide) and kept in tightly stoppered bottles. To begin a run the desired quantity of the adsorbate solution was first neutralized with dilute NH_4OH, made up to 30 gms per liter with distilled water and poured onto the column. By measurement, 25 milliliters of adsorbate solution yielded 1.4337 grams of oxide. Therefore, for a loading of 30 grams, 523 milliliters - equivalent to 29.997 grams of oxide, and for a loading of

15 grams, 262.5 milliliters equivalent to 14.999 grams of oxide were used.

After loading the column, eluent solution was admitted to the top of the column from a constant head tank and the flow rate set by a pinch clamp at the column outlet. This rate was set at approximately 20 milliliters per minute for all runs. Approximately 600 milliliter fractions were collected in the overlap region of Nd and Pr and approximately 1200 milliliter fractions at other periods during the runs. The volume, mean pH, color and time interval of collection were recorded for all fractions and a record was kept of the time at which new batches of eluent solution were added and of the times of shut-down.

Precipitation and Filtration of Fractions

All fractions were checked for rare earths by the addition of 20 ml. of a saturated solution of oxalic acid. In selected fractions yielding a precipitate a sample, extracted before precipitation, was analyzed spectrophotometrically. Each precipitated fraction was allowed to stand overnight before filtering and the filtrate checked in every case for complete precipitation by the addition of 5 milliliters of saturated solution of oxalic acid. Each fraction was filtered through No. 40 Whatman (9 centimeter) ashless paper and the residue washed several times with distilled water.

Ignition of Fractions

The precipitate from each fraction was placed in a

weighed porcelain crucible (size 0) and the paper carefully burned off over a gas flame. The crucible was then covered and fired overnight, or a minimum of six hours, in a muffle furnace at a temperature of 850°C. After firing, the crucible was placed in a dessicator while still warm and allowed to cool. As soon as the crucible was cool, it was weighed to the nearest 0.1 milligram. The fraction was then stored in an appropriately labeled glass vial.

Analysis of Fractions

The analysis was carried out by means of a Beckman DU quartz spectrophotometer (Ser. No. 3204) using absorption peaks at about 446 millimirons for Pr and about 742 and 800 for Nd. Approximately 0.1 grams (weighed to the nearest 0.1 milligram of a fraction of oxide was weighed directly into a clean dry 10 milliliter volumetric flask immediately after the ignition of the oxide was completed. Two milliliters of 2 M HCl was then added to the flask and the flask was warmed to remove any chlorine formed by the reaction of HCl with Pr_6O_{11}. The flask was then filled to the mark with distilled water and mixed throughly by inversion and shaking.

The Corex photometer cells were carefully cleaned by soaking in chromic acid for about ten minutes, thoroughly washing in tap water, and rinsing in distilled water. They were then dried, first with a clean soft cloth, and then by

being placed in the drying oven for about fifteen minutes. The solution for analysis was poured into the clean, dry cell, the cell being filled so as to cover the optical surfaces. These optical surfaces were polished with lens tissue and the cells covered and placed in the cell holder.

The optical densities were determined for each sample at the three peaks by using the technique of scanning to find the peak. The optical densities were also measured at other points such as 400, 650, and 850 millimicrons to determine any background effects. When the optical densities were low, i. e., below about 0.040, it was not always possible to locate the peaks by scanning since the change in sensitivity of the photocell with wave length was greater than the change in absorption. At least two determinations of the optical density at each point were made and all values recorded to the nearest 0.001 unit.

The cell corrections were determined using cell 13957 filled with distilled water as the standard. All cells except this standard were filled with 0.4 M. HCl and the optical densities at and near the various peaks measured. Care was taken that the cells were always placed in the same order and orientation in the cell holder.

Since it has been found that the optical density of a given solution at a given wave length is a function of the slit width used in the measurement, it was necessary to use

a standard slit width for all measurements made at any given wave length. The following table gives the slit widths which were used in all analyses for praseodymium and neodymium.

TABLE III

Standard Slit widths

	Band (mμ)	Slit Widths (mm.)
Neodymium	800	0.0116
	744	0.018
Praseodymium	444	0.0345

The analyses were calculated using the relation $C = D/k$ where C is the concentration of rare earth oxide in gms./ml., and D is the corrected optical density, and k is the extinction coefficient as given in Table IV.

TABLE IV[1]

Extinction Coefficients

Peak (mμ)	k	for peak 800 mμ	
		Conc. Nd_2O_3 (%)	k
446	59.0	20	62.0
744	41.1	40	61.5
800	varies with concentration	60	60.6
		80	59.6
		100	59.3

The corrected optical densities are obtained from the measured optical densities by correcting for the absorption of the cell as related to the standard and for any observed background effects.

A check was made of the absorption of the 5% citric acid solution at 10 mμ intervals over the light range used

---

[1]These slit widths and extinction coefficients are based on the work of Ziegler, W.T., Georgia Institute of Technology Oct. (1949).

in our analyses (400-850 mμ) and no absorption at all was observed. During Run 27, a number of fractions were sampled as they came off the column and the optical densities measured as explained above. The results indicated that the effluent solutions were too dilute to afford an accurate quantitative analysis except possibly for the peak fractions. For example, fraction 21b of Run 27 (Nd peak) gave the following information --- assuming that the extinction coefficients are not effected by this change in the solvent.

Peak	Corr.O.D.	Gms/ml.	Avg.	% in citric acid soln.	% in HCl soln.
800	0.019	0.000321			
744	0.012	0.000292	0.000307	94.8	94.3
444	0.001	0.000017	0.000017	5.2	6.1

Total oxide --550 (0.000324)= 0.178 gms.; by measurement 0.176 gms.

but on the other hand fraction 32b gave this information.

Peak	Corr.O.D.	Gms/ml.	Avg.	% in citric acid soln	% in HCl soln.
800	0.014	0.000235			
744	0.008	0.000195	0.000215	80.8	76.2
444	0.003	0.000051	0.000051	19.2	25.2

Total oxide --550 (0.000266) 0.0149 gms.; by measurement 0.166 gms.

Make up of Eluent Solution

The citric acid eluent solution was made up in 18 liter batches. First 900 grams of citric acid monohydrate (U.S.P.) (50 grams per liter) and 18 grams of phenol (CP) (1 gram per liter) were weighed out and dissolved in 18 liters of distilled water. Next, concentrated ammonium hydroxide was added to obtain the desired pH. The size of the first portion of ammonia was estimated from a chart of pH plotted versus ammonia added so as to give approximately the right pH. The pH was adjusted exactly to that desired by

successively smaller additions. Care was taken that the solution was throughly mixed after each addition. Finally, each batch was tested for precipitable material with oxalic acid before its use. No precipitates were formed.

Before each series of measurements, the pH meter was standardized as follows. First it was set to the correct value reading against a standard buffer[2] of 7.00 with the temperature taken into account. Then, since the general range of measurements was between 3.0 and 4.0, the meter was tested with standard buffer of 4.00 and found to give the correct value of the buffer at the prevailing temperature to within 0.01 pH unit each time.

Calculation of Results

The elution curves for the various runs were obtained as follows:

1. The volume of each fraction was measured to the nearest 5 ml. The weight of oxide contained in each fraction was obtained by weighing the crucibles as soon as they were cool after the ignition of the oxalates to the oxides.
2. From these two values, the concentration of oxide was calculated in grams per liter and plotted against the cumulative volume of eluent.
3. The individual elution curves were obtained by using the results of the spectrophotometric analyses

---

[2]The standard buffers used for the pH meter were from the National Technical Laboratories, South Pasadena, California They were stated to be pH 7.00±0.01 @ 25°C and pH 4.00±0.01

and the total weight per liter to find the weight per liter of the individual rare earth oxides.

For calculation of the material balances, the results of the spectrophotometric analyses were combined with the total weights of oxide per liter to give the individual elution curves as indicated above. These curves were plotted on an enlarged scale. (See Figure 11 for an example) Values of concentration were read from these curves for each oxide and each fraction in the overlap region. The concentrations of Nd and Pr in each fraction were multiplied by the volume of that fraction to obtain the weight of oxide per fraction.

In each run the fractions laying outside the overlap region were assumed to be 100% of the single component and added to the weights per fraction of that component for all the fractions in the overlap region to give the recovery of neodymium and praseodymium oxides (See Tables VII, X, XIII, and XVI.) The lanthanum oxide and cerium oxide weights were obtained simply by adding the weights of the individual fractions containing these substances.

To test this method of calculation, the weights of total oxide, as obtained by the addition of the weights of individual components obtained by this method, were compared with the weights of total oxide obtained by the addition of the actual weights of the fractions.

Run	(1) wt. by calc.	(2) wt. by addition	(1)/(2)
27	29.5313	29.5655	0.9988
28	14.6849	14.7115	0.9982
30	29.1726	29.2054	0.9988
31	14.3583	14.3644	0.9996

Further, the percentage recoveries of the components seemed to be in accord with the total percentage recovery for each run. Thus it is believed that this method of calculation of the material balances of the components gave essentially reliable results.

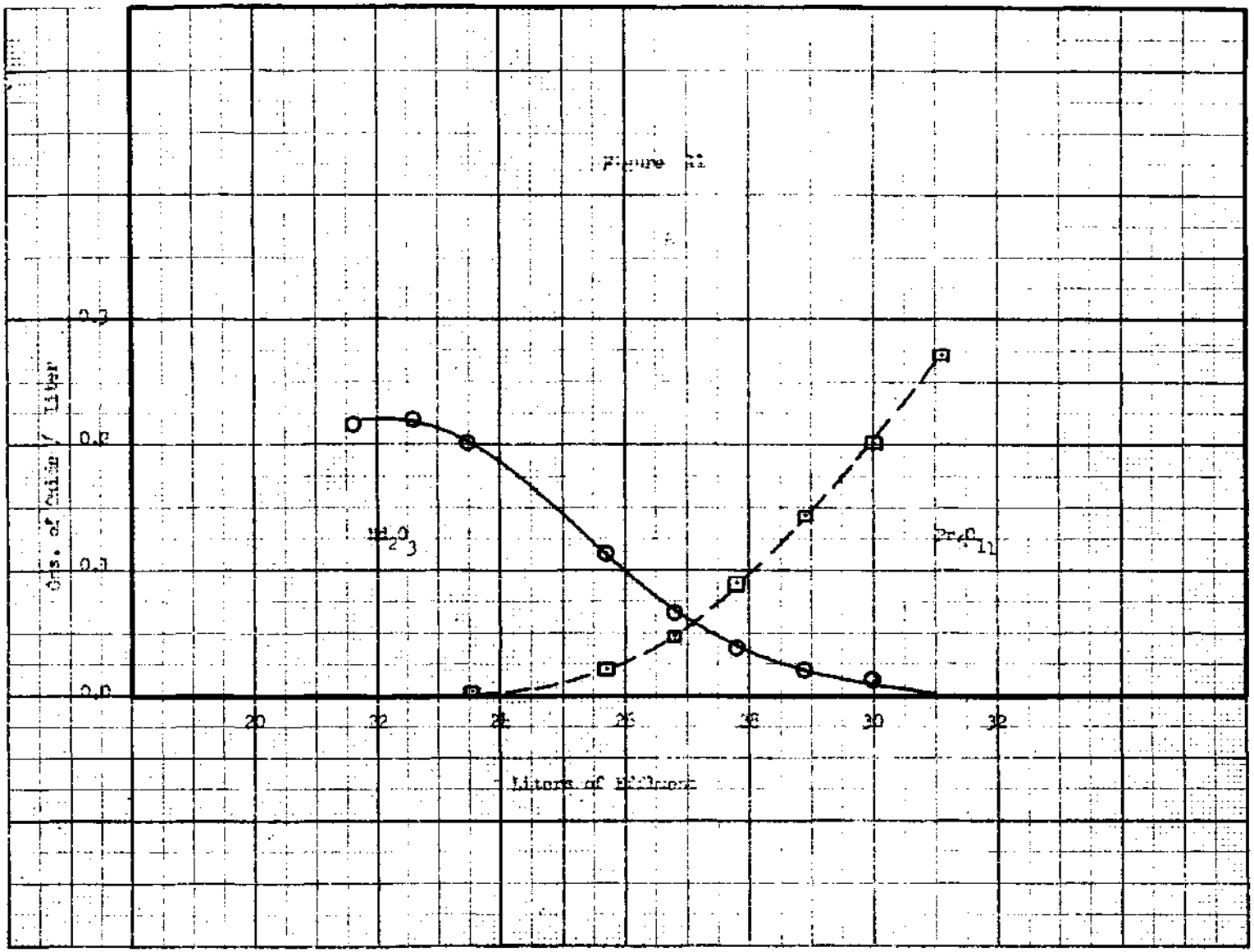
The calculations of the analyses are explained in the section on analysis of the fractions.

FIGURE 11

ENLARGED CURVE OF OVERLAP REGION

Run 28

Nd_2O_3 (⊙) Pr_6O_{11} (⊡)


0.3
0.2
0.1
0.0
20
22
24
26
28
30
32
Fe_2O_3
Pr_6O_{11}

APPENDIX II

TABLE V

SUMMARY OF OPERATION OF COLUMN RUN 27

Column loading - 30.00 gms. Composition of adsorbate

pH adsorbate $\doteq$ 2. 45.1% Pr_6O_{11}, 12.0% Nd_2O_3

Avg. flow rate - 1.09 $\frac{ml_2}{cm\ min}$ 38.2% La_2O_3 , 4.7% CeO_2

Fraction Number	Volume ml.	Mean pH	Wt. of oxide gms per fractions	gms per liter	Color of oxide
A	950	3.63	---	---	---
B	1120	2.84	---	---	---
1	405	3.89	---	---	---
2	1520	3.45	---	---	---
3	1120	2.92	---	---	---
4	1115	2.11	---	---	---
5	1115	3.11	---	---	---
6	1110	3.12	---	---	---
7	1110	3.12	---	---	---
8	1105	3.12	---	---	---
9	1105	3.12	---	---	---
10	1095	3.12	---	---	---
11	1100	3.11	trace	trace	---
12	1095	3.12	0.0202	0.0185	lt tan
13	1100	3.12	0.0558	0.0507	pale blue
14	1090	3.12	0.0999	0.0917	" "
15	1100	3.12	0.1502	0.1365	" "
16a	505	3.12	0.1148	0.2273	blue gray
16b	1530	3.12	0.3672	0.2400	" "
17	1090	3.12	0.2760	0.2532	" "
18a	550	3.12	0.1484	0.2698	lt gray
18b	550	3.11	0.1559	0.2835	lt tan
19a	550	3.11	0.1648	0.2996	" "
19b	550	3.10	0.1671	0.3038	" "
20a	555	3.10	0.1714	0.1088	" "
20b	555	3.10	0.1764	0.3178	" "
21a	560	3.10	0.1796	0.3207	" "
21b	550	3.10	0.1764	0.3207	" "
22a	555	3.10	0.1796	0.3236	gray tan
22b	560	3.10	0.1779	0.3177	tan
* 23a	575	3.10	0.1777	0.3090	lt brown
23b	560	3.10	0.1658	0.2961	" "

* New batch of eluent added to overhead tank during fraction. --- Indicates no oxide obtained from fraction

APPENDIX II

TABLE V (Cont)

Fraction Number	Volume ml.	Mean pH	Wt. of oxide gms per fraction	gms per liter	Color of oxide
24a	570	3.10	0.1668	0.2926	lt brown
24b	570	3.10	0.1926	0.3379	" "
25a	575	3.11	0.1967	0.3421	choc. brown
25b	560	3.11	0.1835	0.3277	" "
26a	570	3.12	0.2070	0.3632	" "
26b	570	3.11	0.2223	0.3900	" "
27a	560	3.11	0.2369	0.4156	" "
27b	560	3.11	0.2473	0.4416	" "
28a	565	3.11	0.2567	0.4543	" "
28b	570	3.11	0.2792	0.4898	" "
29a	570	3.10	0.3064	0.5375	" "
29b	560	3.10	0.3224	0.5757	dk brown
30a	560	3.10	0.3472	0.6200	black
30b	565	3.10	0.3731	0.6604	"
31a	570	3.10	0.3957	0.6942	"
31b	555	3.10	0.4144	0.7467	"
32a	560	3.10	0.4743	0.8470	"
32b	560	3.10	0.4990	0.8911	"
33a	560	3.10	0.4417	0.7888	"
33b	550	3.10	0.5187	0.9431	"
34a	550	3.09	0.5495	0.9991	"
34b	555	3.09	0.5906	1.0641	"
35a	550	3.08	0.5787	1.0522	"
35b	545	3.07	0.6551	1.2020	"
36a	545	3.07	0.6970	1.2789	"
36b	545	3.06	0.7369	1.3521	"
37a	545	3.07	0.7506	1.3772	"
37b	535	3.07	0.7231	1.3516	"
38a	535	3.08	0.6717	1.2555	dk choc brown
38b	540	3.09	0.5910	1.0944	"
39a	540	3.10	0.4731	0.8761	"
39b	540	3.10	0.3315	0.6255	"
**40	1090	3.12	0.3916	0.3593	choc brown
41	1090	3.12	0.3480	0.3193	brick red

** Run stopped for several hours during fraction

APPENDIX II

TABLE V (Cont)

Fraction Number	Volume ml.	Mean pH	Wt. of oxide gms per fraction	gms per liter	Color of oxide
42	1110	3.11	0.3318	0.2989	pink
43	1115	3.11	0.2589	0.2322	lt pink
*44	1130	3.12	0.1723	0.1525	"
45	1110	3.12	0.0983	0.0886	"
46	1110	3.12	0.0515	0.0464	"
47	1105	3.12	trace	trace	---
48	1105	3.12	---	---	---
49	1100	3.12	---	---	---
50	1100	3.12	---	---	---
51	1100	3.13	---	---	---
**52	1050	3.12	---	---	---
***53	1000	3.18	---	---	---
54	1260	3.50	1.8150	1.4405	white
55	1260	3.58	4.4805	3.5567	"
56	1250	3.58	4.5915	3.6732	"
57	1240	3.85	0.2703	0.2180	"
58	1270	3.89	---	---	---
59	1240	3.90	---	---	---
60	1240	3.90	---	---	---

* New batch eluent added to overhead tank during fraction
** Run stopped for several hours during fraction
*** Introduction of pH 3.90 eluent started.
--- Indicates no oxide obtained from fraction.

APPENDIX II

TABLE VI

ANALYSES OF FRACTIONS RUN 27

Run 27 Fraction Number	Weight oxide gm per liter	Percentages Nd_2O_3	Pr_6O_{11}	Total	Wt. Nd_2O_3 gm per liter	Wt. Pr_6O_{11} gm per liter
12	0.0185	88.9	---	88.9	0.0164	---
18a	0.2698	100.0	---	100	0.2698	---
18b	0.2835	100.1%	---	100.1	0.2835	---
19b	0.3038	96.5	2.9	99.4	0.2932	0.0088
21b	0.3207	94.3	6.1	100.4	0.3024	0.0196
23b	0.2961	76.2	25.2	101.4	0.2256	0.0746
25b	0.3277	46.0	55.5	101.5	0.1507	0.1819
26b	0.3900	20.1	81.1	101.2	0.0784	0.3163
27b	0.4416	10.7	89.6	100.3	0.0473	0.3957
28b	0.4898	6.3	96.4	102.7	0.0309	0.4722
29b	0.5757	3.7	95.0	98.7	0.0213	0.5469
31a	0.6942	1.5	100.2	101.7	0.0104	0.6956

APPENDIX II

TABLE VII

MATERIAL BALANCE RUN 27

Fraction Number	Volume ml.	Average Cumulative Volume liters	Nd_2O_3 gms per liter	Nd_2O_3 gms per fraction	Pr_6O_{11} gms per liter	Pr_6O_{11} gms per fraction
12-18b*	550			(1.3884)		
19a	550	20.8	.292	.1606	.004	.0022
19b	550	21.3	.303	.1656	.009	.0050
20a	555	21.9	.306	.1698	.010	.0056
20b	560	22.4	.309	.1715	.011	.0061
21a	550	23.0	.310	.1736	.015	.0084
21b	555	23.5	.304	.1672	.020	.0110
22a	560	24.1	.395	.1637	.030	.0167
22b	575	24.6	.282	.1579	.045	.0252
23a	560	25.2	.260	.1495	.060	.0354
23b	570	25.8	.237	.1327	.085	.0476
24a	570	25.6	.206	.1174	.112	.0638
24b	575	25.9	.182	.1037	.140	.0798
25a	560	27.5	.152	.0874	.171	.0983
25b	570	28.1	.129	.0722	.209	.1170
26a	570	28.6	.108	.0616	.240	.1368
26b	570	29.2	.185	.0485	.278	.1585
27a	560	29.8	.068	.0388	.323	.1835
27b	565	30.3	.053	.0297	.360	.2016
28a	570	30.9	.040	.0226	.404	.2283
28b	570	31.5	.030	.0171	.454	.2588
29a	560	32.0	.026	.0148	.496	.2537
29b	560	32.6	.020	.0112	.550	.3080
30a	565	33.2	.015	.0084	.610	.3416
30b	565	33.7	.010	.0057	.615	.3684
31a-46**						(14.7450)
		Total		3.6396		14.7344

	Nd_2O_3	Pr_6O_{11} - CeO_2	La_2O_3	Total
In	3.5940	14.9171	11.4424	29.9535
Out	3.6396	14.7344	11.1573	29.5313
% recovery	101.3%***	98.8%	97.5 %	98.6%

* Assumed to be pure Nd_2O_3

** Assumed to be pure Pr_6O_{11}

*** High recovery believed due to impurities on the column before the run was started.

APPENDIX II

TABLE VIII

SUMMARY OF OPERATION OF COLUMN RUN 28

Column loading - 15.0 gms. Composition of adsorbate

pH adsorbate - 1.95 45.1% Pr_6O_{11} 12.0% Nd_2O_3

Avg. flow rate - 1.09 $\frac{ml_2}{cm\ min}$ 38.2% La_2O_3, 4.7% CeO_2

Fraction Number	Volume ml.	Mean pH	Wt. of oxide gms per fraction	gms per liter	Color of oxide
A	535	3.62	---	---	---
B	1015	3.00	---	---	---
1	1110	3.90	---	---	---
2	980	3.32	---	---	---
3	965	3.09	---	---	---
4	960	3.12	---	---	---
5	945	3.12	---	---	---
6	945	3.12	---	---	---
7	930	3.12	---	---	---
8	930	3.12	---	---	---
9	930	3.12	---	---	---
10	985	3.12	---	---	---
11	1070	3.12	---	---	---
12	1070	3.12	---	---	---
13	1070	3.12	---	---	---
14	1075	3.12	---	---	---
15	1075	3.12	trace		
16	1135	3.12	.0399	.0351	lt blue
17	1150	3.11	.0802	.0697	" "
18	1150	3.12	.1233	.1072	" "
19	1140	3.12	.1676	.1470	" "
20a	570	3.12	.1000	.1754	" "
20b	575	3.11	.1101	.1914	blue gray
21a	570	3.11	.1176	.2045	" "
21b	570	3.11	.1210	.2123	" "
22a	480	3.11	.1040	.2167	" "
22b	500	3.11	.0874	.2185	" "
23a	400	3.11	.0867	.2168	blue tan
23b	585	3.11	.1196	.2044	" "
24a	545	3.11	.1035	.1899	" "
24b	550	3.11	.0936	.1702	gray tan
25a	550	3.11	.0824	.1498	" "
25b	540	3.11	.0706	.1307	" "

APPENDIX II

TABLE VIII (Cont)

Fraction Number	Volume ml.	Mean pH	Wt. of oxide gms per fraction	gms per liter	Color of oxide
26a	545	3.12	.0647	.1187	choc brown
26b	550	3.12	.0626	.1138	choc brown
27a	550	3.12	.0645	.1173	dk choc brown
28a	540	3.12	.0767	.1420	"
28b	540	3.12	.0892	.1652	"
29a	540	3.11	.1019	.1887	"
29b	535	3.10	.1136	.2123	"
30a	540	3.11	.1300	.2407	"
30b	540	3.11	.1460	.2704	"
31a	540	3.10	.1610	.2981	"
31b	525	3.10	.1723	.3282	"
32a	530	3.10	.1913	.3600	"
32b	535	3.10	.2086	.3869	"
33a	545	3.10	.2236	.4103	"
33b	530	3.10	.2351	.4436	"
34a	530	3.10	.2536	.4785	black
34b	535	3.10	.2713	.5071	"
35a	535	3.10	.2891	.5405	"
35b	525	3.09	.2980	.5676	"
**36	1205	3.09	.7506	.6229	"
37	1115	3.09	.7643	.6855	v dk brown
*38	970	3.09	.6961	.7176	"
39	780	3.10	.5307	.6016	black
40	780	3.12	.4255	.5455	"
41	765	3.12	.2115	.2765	"
42	770	3.12	.0661	.0858	"
43	760	3.12	.0185	.0243	"
44	760	3.12	---	---	---
45	750	3.12	---	---	---
46	750	3.12	---	---	---
47	750	3.12	---	---	---
48	750	3.12	---	---	---
49	715	3.12	.0203	.0284	lt pink
***50	1265	3.12	.2945	.2328	off white
51	1270	3.67	2.0623	1.6239	white
52	1265	3.68	3.1115	2.4597	off white
53	1270	3.80	0.9216	0.7257	pink orange
54	1400	3.89	---	---	---
55	1140	3.89	---	---	---
56	960	3.89	---	---	---

RUN 28

(*) New eluent added to overhead tank during fraction

(**) Run stopped several hours during fraction

(***) Introduction of pH 3.92 eluent started

APPENDIX II

TABLE IX

ANALYSES OF FRACTIONS RUN 28

Run 28 Fraction Number	Weight oxide gm per liter	Percentages			Wt. Nd_2O_3 gm per liter	Wt. Pr_6O_{11} gm per liter
		Nd_2O_3	Pr_6O_{11}	Total		
21b	0.2123	100.9	1.6	102.5	0.2142	0.0034
23b	0.0244	97.5	0.2	97.7	0.1993	0.0004
25b	0.1307	85.1	13.6	98.7	0.1112	0.0178
26b	0.1138	57.3	39.5	96.8	0.0652	0.0450
27b	0.1267	28.5	70.3	98.8	0.0361	0.0891
28b	0.1652	11.5	85.8	97.3	0.0190	0.1417
29b	0.2123	5.2	94.2	99.4	0.0110	0.2000

APPENDIX II

TABLE X

MATERIAL BALANCE RUN 28

Fraction Number	Volume ml.	Average Cumulative Volume	Nd_2O_3 gms per liter	Nd_2O_3 gms per fraction	Pr_6O_{11} gms per liter	Pr_6O_{11} gms per fraction
16-23a*	---	---	0.1993	(1.1378)	---	---
23b	585	23.5	0.182	.1166	0.0004	.0002
24a	545	24.0	0.162	.0992	0.001	.005
24b	550	24.6	0.141	.0801	0.002	.0011
25a	550	25.1	0.1112	.0776	0.010	.0055
25b	540	25.7	0.089	.0600	0.0178	.0096
26a	545	26.2	0.0652	.0485	0.031	.0169
26b	550	26.8	0.050	.0359	0.0450	.0248
27a	550	27.3	0.0361	.0275	0.062	.0341
27b	540	27.8	0.022	.0195	0.0891	.0481
28a	540	28.4	0.0190	.0119	0.115	.0621
28b	540	28.9	0.010	.0103	0.1417	.0765
29a	540	29.5	0.010	.0054	0.170	.0918
29b	535	30.0	0.001	.0054	0.2000	.1070
30a	540	30.5	0.001	.0005	0.239	.1291
30b-43**		---	---	---	---	(5.9222)
		Total		1.7452		6.5295

	Nd_2O_3	Pr_6O_{11}	La_2O_3 -CeO_2	Total
In	1.7996	6.7636	6.4337	14.9969
Out	1.7452	6.5295	6.4102	14.6849
% recovery	97.0	96.5	99.6	97.9

* Assumed to be pure Nd_2O_3
** Assumed to be pure Pr_6O_{11}

APPENDIX II

TABLE XI

SUMMARY OF OPERATION OF COLUMN RUN 30

Column loading - 30.0 gms Composition of adsorbate

pH adsorbate - 2.00 45.1% Pr_6O_{11}, 12.0% Nd_2O_3

Avg. flow rate - 1.07 $\frac{ml_2}{cm\ min}$ 38.2% La_2O_3, 4.7% CeO_2

Fraction Number	Volume ml.	Mean pH	Wt. of oxide gms per fraction	gms per liter	Color of oxide
A	980	3.29	---	---	---
B	970	2.71	---	---	---
1	1270	3.87	---	---	---
2	1100	3.15	---	---	---
3	1080	2.83	---	---	---
4	1050	2.99	---	---	---
5	1035	2.99	---	---	---
6	1010	2.99	---	---	---
7	1000	2.99	---	---	---
8	980	3.00	---	---	---
9	975	3.00	---	---	---
10	955	3.00	---	---	---
11	950	3.00	---	---	---
12	930	3.00	---	---	---
13	940	3.00	---	---	---
14	930	3.00	---	---	---
15	935	3.00	---	---	---
16	930	3.00	---	---	---
17	940	3.00	---	---	---
18	930	3.00	---	---	---
**19	980	3.00	---	---	---
20	1010	3.00	---	---	---
21	1090	2.99	---	---	---
*22	1125	3.00	---	---	---
23	1125	3.00	---	---	---
24	1110	3.00	---	---	---
25	1125	3.00	---	---	---
26	1120	3.00	---	---	---
27	1130	3.00	---	---	---
28	1115	3.00	---	---	---
29	1130	3.00	---	---	---
30	1120	3.00	---	---	---
31	1125	3.00	---	---	---
32	1120	3.00	---	---	---
33	1130	2.99	---	---	---
34	1110	2.99	---	---	---

APPENDIX II

TABLE XI (Cont)

Fraction Number	Volume ml.	Mean pH	Wt. of oxide gms per fraction	gms per liter	Color of oxide
*35	1170	3.00	---	---	---
36	1170	2.99	---	---	---
37	1200	3.00	---	---	---
38	1185	3.00	---	---	---
39	1190	3.00	---	---	---
40	1190	2.99	---	---	---
41	1195	2.99	---	---	---
42	1180	2.99	---	---	---
43	1190	2.99	trace	trace	
44	1180	2.99	.0260	.0220	lt blue
45a	610	2.99	.0275	.0450	"
45b	615	2.99	.0440	.0715	"
46a	610	2.99	.0523	.0857	"
46b	620	2.99	.0709	.1144	"
*47a	590	2.99	.0843	.1429	"
47b	535	2.99	.0916	.1712	"
48a	550	2.98	.1119	.2034	"
48b	570	2.96	.1332	.2337	"
49a	570	2.96	.1545	.2711	"
49b	570	2.95	.1767	.3100	"
50a	560	2.95	.1938	.3461	"
50b	570	2.94	.2152	.3775	v lt blue
51a	565	2.94	.2303	.4076	lt blue
51b	570	2.92	.2366	.4098	lt blue
52a	560	2.92	.2429	.4338	"
52b	570	2.92	.2423	.4251	"
53a	570	2.92	.2308	.4049	"
53b	570	2.94	.2094	.3674	gray blue
54a	560	2.94	.1800	.3214	"
54b	565	2.94	.1526	.2701	"
55a	565	2.95	.1228	.2173	"
55b	565	2.96	.0994	.1759	gray tan
56a	560	2.96	.0812	.1450	"
56b	565	2.98	.0781	.1382	lt tan
57a	565	2.97	.1031	.1825	choc brown
57b	565	2.95	.1569	.2777	"
58a	560	2.93	.2386	.4261	dk choc brown
58b	565	2.91	.3385	.5991	"
59a	565	2.90	.4308	.7625	"
59b	570	2.90	.4946	.8677	black
60a	555	2.90	.5244	.9449	"
60b	565	2.90	.5443	.9634	"
61a	565	2.90	.5478	.9696	"
61b	570	2.90	.5439	.9542	"

APPENDIX II

TABLE XI (Cont)

Fraction Number	Volume ml.	Mean pH	Wt. of oxide gms per fraction	gms per liter	Color of oxide
62a	560	2.90	.5201	.9288	black
62b	565	2.90	.5159	.9131	"
63	1125	2.90	.9622	.8553	"
64	1110	2.90	.8934	.8049	"
65	1120	2.91	.8268	.7382	"
66	1105	2.92	.7430	.6724	v dk brown
67	1115	2.92	.6713	.6021	"
*68	1155	2.92	.6174	.5345	"
69	1160	2.92	.5416	.4669	"
70	1115	2.93	.4564	.4093	"
**71	1110	2.93	.4004	.3607	"
72	1130	2.95	.3418	.3025	"
73	1150	2.99	.2876	.2501	dk brown
74	1130	2.99	.2376	.2103	"
75a	575	2.99	.1069	.1895	"
75b	575	3.00	.0970	.1687	"
76a	565	3.00	.0866	.1533	"
76b	570	3.00	.0798	.1400	"
77a	575	3.00	.0718	.1249	"
77b	575	3.00	.0656	.1141	"
*78a	570	3.00	.0598	.1049	"
78b	595	3.00	.0492	.0841	"
79a	595	3.00	.0569	.0956	"
79b	585	2.99	.0451	.0771	"
80a	580	3.00	.0408	.0703	"
80b	580	3.00	.0383	.0660	"
81a	520	3.00	.0335	.0644	"
81b	225	3.00	.0143	.0636	"
82a	170	3.00	.0103	.0606	"
82b	325	3.00	.0237	.0729	"
83a	505	3.02	.0096	.0190	"
83b	420	3.07	---	---	---
84a	520	3.00	.0126	.0242	dk brown
84b	600	3.00	.0181	.0302	"
85a	580	3.00	.0189	.0326	"
85b	570	3.00	.0156	.0274	"
86	1020	3.00	trace		
87	1095	3.00	trace		
88	1080	3.00	trace		
89	1040	3.00	trace		
90	1040	3.00	trace		

APPENDIX II

TABLE XI (Cont)

Fraction Number	Volume ml.	Mean pH	Wt. of oxide gms per fraction	gms per liter	Color of oxide
91	1020	3.00	---	---	
92	1020	3.01	---	---	
93	1105	3.00	---	---	
94	1140	3.00	---	---	
95	1115	3.00	---	---	
96	1130	3.00	---	---	
97	1115	3.00	---	---	
98	1120	3.00	---	---	
99	1110	3.00	---	---	
*100	1100	3.00	----	---	
101	1160	3.00	---	---	
102	1180	3.00	---	---	
103	1160	3.00	---	---	
104	1155	3.00	---	---	
105	1140	3.00	---	---	
106	1140	3.00	---	---	
107	1130	3.00	---	---	
108	1150	3.00	---	---	
109	1130	3.00	---	---	
110	1135	3.00	---	---	
111	1120	3.00	---	---	
112	1100	3.00	---	---	
***113	1215	3.00	---	---	
114	1230	3.48			
115	1220	3.59	12.8243		white
116	1180	3.52			
117	1160	3.80			
118-123	6475	3.89	---	---	

Run 30

(*) New batch of eluent added to overhead tank during fraction
(**) Run stopped several hours during fraction
(***) Introduction of pH 3.89 eluent started
(****) Machine did not change flasks, small amount spilt

APPENDIX II

TABLE XII

ANALYSES OF FRACTIONS RUN 30

Run 30 Fraction Number	Weight oxide gm per liter	Percentages			Wt. Nd_2O_3 gm per liter	Wt. Pr_6O_{11} gm per liter
		Nd_2O_3	Pr_6O_{11}	Total		
45b	0.0715	100.0	---	100.0	0.0715	---
52a	0.4338	100.0	---	100.0	0.4338	---
54a	0.3214	97.2	1.2	98.4	0.3214	0.0039
55a	0.2173	96.0	2.4	98.4	0.2086	0.0052
56b	0.1450	65.0	35.0	100.0	0.0943	0.0517
57b	0.2777	15.3	84.3	99.6	0.0425	0.2341
58b	0.5991	3.2	96.9	100.1	0.0192	0.5805
59b	0.8677	1.0	98.9	99.9	0.0087	0.8582
81	0.0641	---	101.9	101.9	---	0.0653

APPENDIX II

TABLE XIII

MATERIAL BALANCE RUN 30

Fraction Number	Volume ml.	Average Cumulative Volume liters	Nd_2O_3 gms per liter	Nd_2O_3 gms per fraction	Pr_6O_{11} gms per liter	Pr_6O_{11} gms per fraction
44-52a*	---	---	---	(2.0917)	---	---
52b	570	56.4	.425	.2423	.000	.0006
53a	570	57.0	.405	.2309	.000	.0022
53b	570	57.5	.366	.2086	.001	.0023
54a	560	58.1	.312	.1747	.0039	.0028
54b	565	58.7	.253	.1429	.004	.0057
55a	565	59.2	.208	.1175	.005	.0147
55b	565	59.8	.1153	.0864	.010	.0311
56a	560	60.3	.119	.0666	.025	.0746
56b	565	60.9	.089	.0503	.055	.1345
57a	565	61.5	.060	.0339	.132	.2251
57b	565	62.0	.040	.0226	.238	.3164
58a	560	62.6	.024	.0134	.402	.4271
58b	565	63.2	.011	.0062	.560	.4891
59a	565	63.7	.006	.0034	.756	
59b	570	64.3	.002	.0011	.858	
60a*85**						11.1303
			Totals	3.4925		12.8558

	Nd_2O_3	Pr_6O_{11}	La_2O_3 - CeO_2	Total
In	3.5934	13.5092	12.8503	29.9540
Out	3.4925	12.8558	12.8243	29.1726
% recovery	97.2%	95.2%	99.8%	97.4%

* Assumed to be pure Nd_2O_3
** Assumed to be pure Pr_6O_{11}

APPENDIX II

TABLE XIV

SUMMARY OF OPERATION OF COLUMN RUN 31

Column loading - 15.0 gms. Composition of adsorbate

pH adsorbate - 3.05 45.1% Pr_6O_{11}, 12.0% Nd_2O_3

Avg. flow rate - 1.09 $\frac{ml^2}{cm\ min}$ 38.2% La_2O_3, 4.7% CeO_2

Fraction Number	Volume ml.	Mean pH	Wt. of oxide gms per fraction	gms per liter	Color of oxide
A	575	5.01	---	---	
B	1005	2.99	---	---	
1-3	3670	2.99	---	---	
4	1120	3.00	---	---	
5	1120	3.00	---	---	
6	1105	3.00	---	---	
7	1110	3.00	---	---	
8	1090	3.00	---	---	
9	1100	3.00	---	---	
10	1080	3.00	---	---	
11	1090	3.00	---	---	
12	1080	3.00	---	---	
13	1090	3.00	---	---	
14	1080	3.00	---	---	
*15	1090	3.00	---	---	
16	1090	3.00	---	---	
17	1090	3.00	---	---	
18	1085	3.00	---	---	
19	1090	3.00	---	---	
20	1085	3.00	---	---	
21	1100	3.00	---	---	
22	1085	3.00	---	---	
23	1100	3.00	---	---	
**24	1100	3.00	---	---	
25	1120	3.00	---	---	
26	1095	3.00	---	---	
27	1100	3.00	---	---	
28	1090	3.00	---	---	
29	1095	3.00	---	---	
30	1080	3.00	---	---	
31	1090	3.00	---	---	
32	1075	3.00	---	---	
33	1080	3.00	---	---	
34	1075	3.00	---	---	

APPENDIX II

TABLE XIV (Cont)

Fraction Number	Volume ml.	Mean pH	Wt. of oxide gms per fraction	gms per liter	Color of oxide
35	1075	3.00	---	---	
36	1060	3.00	---	---	
37	1075	3.00	---	---	
38	1060	3.00	---	---	
39	1070	3.00	---	---	
40	1055	3.00	---	---	
41	1075	3.00	---	---	
42	1065	3.00	trace		
**43	1110	3.00	.0195	.0176	lt blue
44	1090	3.00	.0480	.0440	"
45	1060	3.00	.0738	.0606	"
46a	575	3.00	.0522	.0908	"
46b	610	3.00	.0653	.1070	"
47a	590	3.00	.0726	.1231	"
47b	590	3.00	.0777	.1317	"
48a	580	3.00	.0876	.1510	"
48b	590	3.00	.0954	.1617	"
49a	590	2.99	.1002	.1698	"
49b	590	2.99	.1014	.1763	"
50a	575	2.99	.1014	.1739	"
50b	590	2.99	.1026	.1739	"
51a	590	2.99	.1002	.1698	"
51b	585	2.99	.0953	.1629	"
52a	570	2.99	.0875	.1535	"
52b	580	2.99	.0815	.1405	"
53a	575	2.99	.0738	.1272	"
53b	580	2.99	.0636	.1106	"
54a	570	3.00	.0531	.0932	"
54b	570	3.00	.0459	.0785	"
55a	580	3.00	.0373	.0643	"
55b	580	3.00	.0308	.0531	blue tan
56a	565	3.00	.0367	.0473	"
56b	580	3.00	.0238	.0410	lt blue
57a	580	3.00	.0248	.0428	dk brown
58a	580	3.00	.0563	.0907	"
58b	580	3.00	.0738	.1272	"
59a	580	2.99	.0963	.1660	"
59b	580	2.99	.1025	.1814	"
60a	600	2.99	.1330	.2217	v dk brown
***60b	565	2.99	.1025	.1814	"
61	1190	2.99	.3425	.2878	"

APPENDIX II

TABLE XIV (Cont)

Fraction Number	Volume ml.	Mean pH	Wt. of oxide gms per fraction	gms per liter	Color of oxide
62	1175	3.97	.4324	.3680	v dk brown
63	1190	2.95	.5446	.4576	"
64	1185	2.94	.5888	.4696	"
65	1190	2.92	.6552	.5506	"
66	1170	2.92	.5803	.4970	"
67	1185	2.95	.4462	.3765	"
68	1165	2.96	.4190	.3597	"
69	1180	2.96	.3545	.3005	"
70	1180	2.98	.2888	.2468	"
71	1186	2.99	.2490	.2101	"
72	1165	2.99	.2037	.1748	"
73	1175	2.99	.1689	.1437	"
74	1160	2.99	.1235	.1065	"
75	1165	3.00	.1127	.0967	"
76	1145	3.00	.0901	.0787	"
77	1155	3.00	.0720	.0623	"
78	1140	3.00	.0553	.0485	black
79	1150	3.00	.0402	.0350	v dk brown
80	1130	3.00	.0414	.0366	"
81	1140	3.00	.0305	.0268	black
82	1120	3.00	.0177	.0158	"
83	1140	3.00	trace		
84-5	2140	3.00	trace		
86	1125	3.00	---	---	
87	1120	3.00	---	---	
88	1115	3.00	---	---	
89	880	3.00	---	---	
90	1150	3.00	---	---	
91	1180	3.19	---	---	
92	1140	3.20	---	---	
93	1150	3.19	---	---	
94	1150	3.19	---	---	
95	1150	3.19	.0754	.0656	pink
96	1125	3.19	.1245	.1107	v lt pink
97	1140	3.19	.1567	.1375	off white
98	1115	3.19	.1482	.1329	"
99	1130	3.19	.1112	.0984	pink
100	1100	3.19	.0664	.0604	v lt pink
101	1125	3.19	.0180	.0160	brick red
102	1105	3.20	---	---	
103	1120	3.19	---	---	
104	1110	3.19	---	---	
105	1125	3.19	---	---	

APPENDIX II

TABLE XIV (Cont)

Fraction Number	Volume ml.	Mean pH	Wt. of oxide gms per fraction	gms per liter	Color of oxide
106	1115	3.19	---	---	
107	1125	3.19	---	---	
******108	1280	3.21	---	---	
109	1300	3.65			
110	1270	3.79	5.5853		white
111	1275	3.93			
112	1235	3.94	---	---	
113	1235	3.94	---	---	
114	1235	3.94	---	---	
115	1205	3.94	---	---	
116	1160	3.94	---	---	

(*) New eluent added to overhead tanks during fraction
(**) Recycle eluent added to overhead tank during fraction
(***) Run stopped several hours during fraction
(****) Introduction of pH 3.20 eluent started
(*****) Introduction of pH 3.94 eluent started

APPENDIX II

TABLE XV

ANALYSES OF FRACTIONS RUN 31

Run 31 Fraction Number	Weight oxide gm per liter	Percentages Nd_2O_3	Percentages Pr_6O_{11}	Percentages Total	Wt. Nd_2O_3 gm per liter	Wt. Pr_6O_{11} gm per liter
54b	0.0875	99.4	1.9	101.3	0.0870	0.0015
55b	0.0531	93.6	8.0	101.6	0.0497	0.0042
56a	0.0473	88.9	17.5	102.4	0.0402	0.0083
56b	0.0410	65.1	35.6	100.7	0.0267	0.0146
57b	0.0609	28.1	71.0	99.1	0.0171	0.0432
58b	0.0907	8.9	91.3	100.2	0.0081	0.0828
59b	0.1660	3.4	97.2	100.6	0.0056	0.1614

APPENDIX II

TABLE XVI

MATERIAL BALANCE RUN 31

Fraction Number	Volume ml.	Average Cumulative Volume liters	Nd_2O_3 gm per liter	Nd_2O_3 gm per fraction	Pr_6O_{11} gm per liter	Pr_6O_{11} gm per fraction
43-45a*	---	---	---	(1.5542)	---	---
54b	585	59.5	.078	.0456	.002	.0012
55	580	60.1	.060	.0348	.003	.0017
	580	60.7	.050	.0290	.004	.0023
56	565	61.3	.040	.0226	.008	.0045
	580	61.9	.027	.0157	.015	.0083
57	580	62.4	.021	.0122	.020	.0116
	580	63.0	.017	.0099	.042	.0249
58	570	63.6	.010	.0057	.061	.0348
	580	64.2	.008	.0046	.083	.0481
59	580	64.7	.007	.0041	.115	.0667
	580	65.3	.006	.0035	.161	.0034
60a-82**						(6.0928)
		Total		1.7419		6.3907

	Nd_2O_3	Pr_6O_{11}	La_2O_3	CeO_2	Total
In	1.7996	6.7636	5.7289	.7004	14.9925
In	1.7419	6.3907	5.5853	.7004	14.4183
% recovery	96.8%	94.5%	97.5%	100% ***	96.2%

* Assumed to be pure Nd_2O_3
** Assumed to be pure Pr_6O_{11}
*** The recovery of CeO_2 on this run is taken as the analysis for this oxide on the adsorbate mixture.

APPENDIX II

TABLE XVII

SUMMARY OF COLUMN OF OPERATION RUN 33

Column loading - 30.0 gms.

pH adsorbate - 2.30

Composition of adsorbate

45.1% Pr_6O_{11} , 12.0% Nd_2O_3

38.2% La_2O_3 , 4.7% CeO_2

Fraction Number	Volume ml.	Mean pH	Wt. of oxide gms per fraction	gms per liter	Color of oxide
A	825	3.60	---	---	
B	890	2.80	---	---	
1	1175	3.90	---	---	
2	1070	3.28	---	---	
3	1060	2.98	---	---	
4	1050	3.12	---	---	
5	1050		---	---	
6	1045	3.12	---	---	
7	1050		---	---	
8	1040	3.12	---	---	
9	1050		---	---	
10	1035	3.12	---	---	
11	1040		---	---	
12	1030	3.12	---	---	
13	1030		---	---	
14	1030	3.12	No ppt.	---	
15*****	1030	3.12	.0360	.0350	lt blue
16	1010	3.11	.0775	.0767	"
17	1135		.1457	.1284	"
18	1140	3.10	.2087	.1831	"
19	1140	3.11	.2711	.2378	"
20	1140		.3394	.2977	"
21*	1190	3.10	.4048	.3402	"
22	1180		.4672	.3959	"
23	1180	3.09	.5500	.4661	"
24	1180		.5104	.4325	"
25	1180	3.10	.2644	.2241	"
26	1180	3.12	.0642	.0544	"
27	1180		trace		
28* **	1110	3.12	---	---	
29	815		---	---	
30	815	3.12	---	---	
31	810		---	---	
32	800	3.12	---	---	
33	795		---	---	
34 ***	1370	3.18	No.ppt.		

APPENDIX II

TABLE XVII (Cont)

Fraction Number	Volume ml.	Mean pH	Wt. of oxide gms per fraction	gms per liter	Color of oxide
35	1190	3.72	2.4945	2.0962	white
36	950	3.68	3.0514	4.0008	"
37****	1105	3.61	4.1008	4.7225	"
38	1010	3.59	4.7997	4.7225	"
39	1000	3.51	5.2947	5.2947	"
40	990	3.52	4.9572	5.0073	"
41	990	3.78	2.1646	2.1895	"
42*****	1095	3.93	0.0216	0.0197	"
43	1100	3.95	No ppt.	---	
44	1080	3.95	---	---	
45	1070	3.95	---	---	

* New eluent solution pH 3.12 added to overhead bottle
** Air bubble formed in feed line
*** Introduction of pH 3.95 eluent started
***** Flow rate effluent adjusted.

Note: Fractions 15-26 all oxides were light blue
Fractions 35-42 all oxides were white

APPENDIX II

TABLE XVIII

MATERIAL BALANCE OF RUN 33

	Nd_2O_3	La_2O_3	Total
In	3.60	26.40	30.00
Out	3.3394 *	26.8545 **	30.1939
Per cent recovery	93.8%	101.7%	100.6%

* Fractions 15-26 assumed to be pure Nd_2O_3
** Fractions 35-42 assumed to be pure La_2O_3

APPENDIX II

TABLE XIX

SUMMARY OF COLUMN OF OPERATION RUN 34

Column loading 3.6 gms

pH adsorbate - 2.89

Avg. flow rate - 1.08 $\frac{ml2}{cm.min}$

Composition of adsorbate

45.1% Pr_6O_{11} , 12.0% Nd_2O_3

38.2% La_2O_3 , 4.7% CeO_2

Fraction Number	Volume ml.	Mean pH	Wt. of oxide gms per fractions	gms per liter	Color of oxide
A	285	600	---	---	
B	970	3.75	---	---	
1	970	3.94	---	---	
2	885	3.49	---	---	
3	900	3.12	---	---	
4	870	3.12	---	---	
5	910	3.12	---	---	
6	1110		---	---	
7	1170	3.12	---	---	
8	1140		---	---	
9	1150	3.12	---	---	
10	1125		---	---	
11 (*)	1150	3.12	---	---	
12	1135		---	---	
13	1140	3.12	---	---	
14	1110		---	---	
15	1125	3.12	trace		
16	1100		.0541	.0492	lt blue
17	1120	3.12	.1042	.0930	"
18	1090		.1500	.1467	"
19	1105	3.11	.2215	.2005	"
20	1130		.2780	.2460	"
21	1110	3.10	.3375	.3068	"
22	1075		.3924	.3650	"
23	1085	3.10	.4569	.4173	"
24	1065		.4877	.4579	"
25	1140	3.10	.4440	.3895	"
26	1165		.3042	.2856	"
27	1080	3.12	.1657	.1534	"
28	1070		.0559	.0527	"
29	1080	3.12	No ppt.		
30	1055		---	---	
31	1070	3.12	---	---	
32	1055	3.12	---	---	
			Total recovery 3.4620 gms.		96.2%

(*) New eluent pH 3.12 added to overhead tank
Note: All oxides obtained were light blue

--- Indicates no oxide obtained from fraction.

APPENDIX II

TABLE XX

SAMPLE CALCULATION OF PURITY OF RECOVERED OXIDES

RUN - 24 95% Purity

	Wt. of Nd_2O_3 from fraction (gms)	Total wt. of fraction (gms)	% purity of fraction
Fractions 15-18*	(0.9358)	(0.9358)	(100%)
19	0.344	0.3494	99.7%
20	0.364	0.3730	97.5%
21	0.346	0.3642	95.0%
	1.990	2.0224	

Total wt. of Nd_2O_3 recovered in the run 2.771 gms.

% oxide of 95% purity = $\frac{2.0224}{2.771}$ = 73%

Note: Fraction 22 was only 87% Nd_2O_3

* Fractions assumed to be pure Nd_2O_3.